TEXTILE RESEARCH JOURNAL

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VOLUME XXVIII OCTOBER 1958 NUMBER 10

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number 6, October, 1958

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Control—No Exposure		1.20	6.82	8.23	1.71	4.35	1.76
175	100	1.2	6.7	7.9	1.6	4.4	—
175	320	1.2	6.9	7.7	1.7	4.2	—
175	1000	1.1	6.8	8.0	1.5	4.2	—
175	1800	1.1	6.8	7.8	1.9	4.1	—
250	10	1.1	—	8.4	—	4.3	—
250	32	1.2	6.9	8.3	1.6	4.2	—
250	100	1.2	6.7	8.2	1.8	4.0	—
250	320	1.2	6.8	7.9	1.6	3.6	—
250	1000	0.9	6.8	7.1	1.7	2.8	—
250	1800	0.8	6.8	6.5	1.8	2.1	—
350	1	1.2	6.8	8.0	1.6	4.2	1.8
350	3.2	1.1	—	7.6	—	3.1	—
350	10	1.1	6.5	7.6	1.6	2.6	1.8
350	18	1.0	—	6.2	1.6	1.7	—
350	32	1.0	5.1	6.0	1.3	1.6	—
350	56	0.8	5.1	4.4	1.0	1.2	—
350	100	0.7	4.7	2.6	0.9	0.7	1.7
350	180	D	3.2	1.4	0.3	0.5	—
350	320	D	2.9	0.9	D	D	1.8
350	1000	D	2.9	—	D	—	1.7
350	1800	D	2.8	—	D	—	1.8
425	0.01	1.2	6.7	8.0	1.7	4.2	1.7
425	0.03	1.0	—	8.0	1.4	4.1	—
425	0.10	1.1	—	8.2	1.5	4.1	1.7
425	0.32	0.9	6.2	7.5	1.5	3.7	—
425	1.00	0.7	5.8	6.9	1.5	2.5	1.7
550	1	—	—	—	—	—	1.5
550	10	—	—	—	—	—	1.6
550	100	—	—	—	—	—	1.6
550	1000	—	—	—	—	—	1.2

- Data shown here were obtained for Du Pont by the Lowell Technological Institute Research Foundation.
- "D" is used to designate yarns too weak to test.
- † Breaking strengths were determined at 70°F., 65% R.H. on an Instron Tensile Tester.
- The breaking strength in grams was divided by the denier of the control sample to obtain the breaking tenacity in grams per initial denier.

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IN THIS ISSUE

The Evaluation of the Spinning Properties of Man-Made Staple Fibers. *H. L. Röder* 819

A Comparison of the Three Methods (Single and Dougle Rip) for the Determination of Tearing Strength of Fabrics. *L. H. Turl* 839

Comparison of Methods for Determining Intrinsic Viscosities from Non-Newtonian Viscosities. *K. H. Cram and J. C. Whitwell* 849

Topochemical Mechanisms Involved in the Preparation and Deacetylation of Partially Acetylated Cottons. *August V. Bailey, Edith Honold, and Evald L. Skau* 861

The Fate of Thioglycollic Acid in Wool Durably Creased with Thioglycollate. *P. H. Springell* 874

Change of Cross-Sectional Area of Single Jute Filaments with Relative Humidity. *A. C. Chakravarty* 878

A Wear Study of the Serviceability of a Minimum Care Garment. *Mary Ann Morris and Barbara Wilsey*

Part I: Subjective Evaluation 881

Part II: Laboratory Evaluation 887

The Application of Spot Tests in the Examination of Synthetic Fibers. Part I. *Fritz Feigl, Vincente Gentil, and Erwin Jungreis* 892

LETTERS TO THE EDITOR

Iodine Sorption Values of Some Chemically Modified Cottons. *August V. Bailey, Edith Honold, and Evald L. Skau* 895

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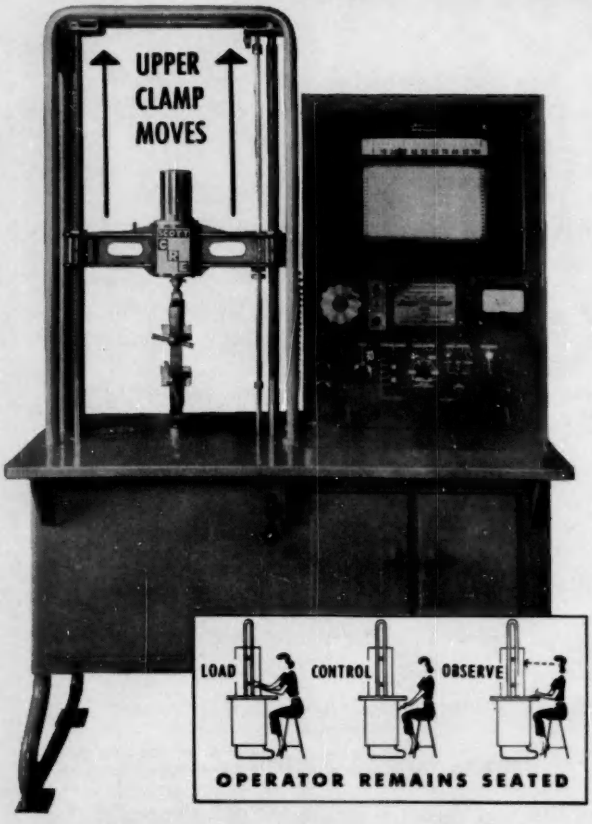

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TEXTILE RESEARCH JOURNAL

The Evaluation of the Spinning Properties of Man-Made Staple Fibers[1]

H. L. Röder

N. V. Onderzoekingsinstituut "Research," Arnhem, Holland

Abstract

A survey is given of the five properties of individual fibers which determine behavior during processing—length, thickness, geometrical structure, surface layer, and the inside structure of the fiber. The geometrical structure consists of three elements: the length structure, the cross-sectional structure, and the surface structure.

The existing spinning techniques have been based on length and thickness of the fibers. The complete conversion of fibers into yarns is divided into two main operations: those which lead to the formation of a card sliver and those which convert the card sliver into a yarn. The criteria for normal processing on the cotton system and on the worsted system are mentioned and illustrated with some data.

The methods used for measurement of these fiber properties are described. They are subdivided into two categories: those by which properties of *one* fiber are measured and those by which the effect of the interaction of fibers is measured.

Special attention is paid to those measuring techniques which have originally been developed in the Textile Research Department of the "Algemene Kunstzijde Unie," *viz.*, equipment for measuring fiber length, linear density, crimp, surface friction, and stiffness (all of individual fibers) and equipment for determining sliver strength and drafting forces for assemblages of fibers.

The behavior of fibers during processing is determined by their interactions. For this reason the determination of drafting forces is most effective in studying processing qualities of fibers. It is demonstrated that man-made fibers exhibit relatively large drafting forces at drafts between 1.2 and 1.8.

In this region drafting forces are much larger than those with cotton and probably those with wool fibers. Therefore, in the processing of man-made fibers, "breaking-draft" zones should be avoided. This is illustrated by the improvements brought about by two-line drafting on drawing frames, two-zone drafting on slubbing and roving frames, and elimination of the top-rollers on the back cylinder in the spinning machines of the cotton system when processing rayon polyamide and polyester fibers. A relation exists between the coefficients of friction of a staple fiber, the drafting forces as measured on the instrument, and the behavior of fibers during the conversion of slivers into yarns in actual processing.

[1] Presented at the joint conference of The Fiber Society and the Textile Institute, Boston, Mass., September 4-6, 1957.

Introduction

In this paper the spinning properties of man-made staple fibers will be considered mainly from the point of view of the producer of these fibers who wants to know if his product can be spun without difficulties. There is a typical difference in approach between the consumer of natural fibers in the textile industry and the producer of man-made fibers. The consumer of natural fibers accepts them as they are and has at his disposal machinery which suits the various types of fibers and which is adaptable to the variations always occurring in them. As soon as the fibers exhibit a variation compared with previous lots, the spinner will start to change gears, thus modifying twists or drafts, etc.; in doing so he will adapt the machines to the raw material.

The producer of man-made fibers, however, has to take existing spinning machinery as a constant factor to which he has to adapt the fibers he is producing. As soon as the fiber exhibits a difference compared with previous lots, he will start to change the finish, the crimp, the degree of opening, or whatever factor may lend itself for change, and in doing so the fiber is adapted to the existing machines.

The designers of spinning machinery have started to develop new machinery specially intended for taking into account the characteristic properties of man-made fibers: in the last 20–30 years quite a range of new machines has already been developed: long staple ($2\frac{1}{2}$ in.) cotton system drawing, roving, and spinning frames were among the first in this line, followed by the whole range of tow to top and direct spinning machines, etc.

Also, a tendency has been made to modify the properties of natural fibers along lines indicated by the man-made fiber industry, thus trying to simplify or improve the processing methods of the natural fibers.

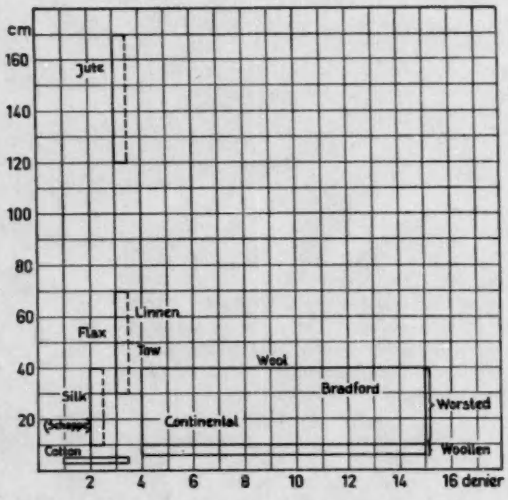

Fig. 1. Schematic classification of spinning systems.

General Observations

The behavior of staple fibers in relation to conversion into yarns is mainly governed by the length, thickness, geometrical structure (these three determine the form), surface layer, and inside of the fiber.

In the processing of staple fibers the form plus the surface layer is considered to be of primary importance and the inside of the fiber to be of secondary value. Of course, from the point of view of end-use appreciation, a different order would be relevant.

Length and Thickness

Length and thickness of a fiber are of so much importance that all the existing spinning systems may be classified according to length and thickness of the fiber for which they are meant. For historical reasons the various spinning systems are usually identified by the fibers for which they have been developed. In Figure 1 they have been schematically classified according to the length and thickness of the fibers.

The cotton spinning systems are intended for the shortest and finest natural fibers (length of 20–40 mm. and fineness of 1–3.5 den.). The silk (Schappe) system is intended for relatively long but fine fibers (up to about 400 mm.; thickness above 2 den.).

Flax and jute systems are intended for long fibers (up to 1–2 m.) of varying fineness, the actual fineness being governed by the amount of splitting of the rather coarse constituents into their finer basic elements brought about during preparation of the fiber (retting for flax, batching for jute, etc.).

The woolen and worsted spinning systems have been developed for wool fibers (of 60–400 mm. and thickness of 4–16 den.). For the shorter types the woolen system is applied and for the longer fibers the worsted system (the Bradford system for the coarser types or the continental system for the finer types).

As in the wool-processing machines, in cotton processing there are two types of spinning equipment depending on the length of the fibers—the cotton-waste type spinning machines for the shorter fibers and the three and four cylinder type machines often combined with a combing passage for the longer fibers. This has been schematically indicated in Figure 2.

The "amount of difficulty" or "subtleness" of these various spinning systems increases on approaching the spinning systems in the lower left corner of Figure 1; i.e., the short, fine fibers as supplied by the cotton plant are the least easy for conversion into yarns.

On the other hand, the long coarse fibers (i.e., bast and wool fibers) are easier to spin into yarns. Although, in the daily practice of a mill, spinners may differ on this point, nevertheless experience with processing of man-made fibers shows that when a new fiber is introduced it is safe to start with a high denier and a long staple (i.e., the woolen or the worsted system). When experience with these fibers has been gained in that sector the product may carefully proceed to the lower deniers and the shorter staple lengths.

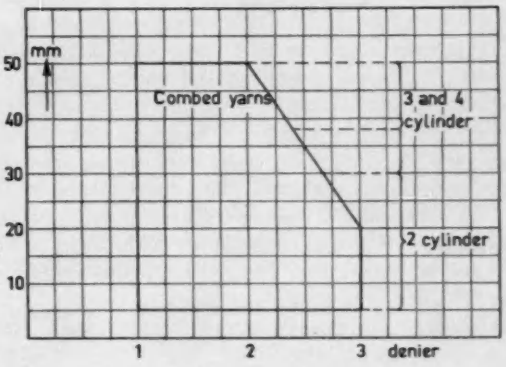

Fig. 2. Details of cotton spinning systems.

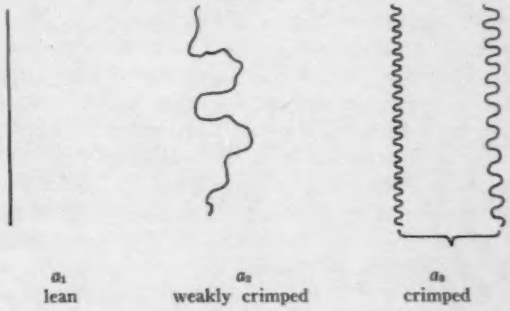

Fig. 3. Schematic representation of length structure of fibers.

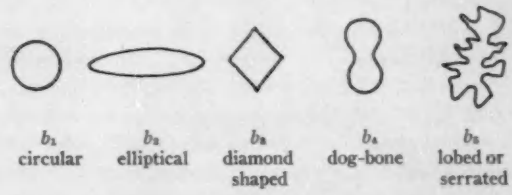

Fig. 4. Schematic representation of some characteristic cross sections of fibers.

The Geometrical Structure

The geometrical structure of a fiber is composed of three different elements.

The Length Structure

This indicates the overall shape of the fiber in the direction of its axis (i.e., "waviness" or crimp); speaking in general, its deviation from a straight line. Several schematic cases may be distinguished (Figure 3).

The Cross-Sectional Structure

The cross section of a fiber is of very great importance. It may vary from a perfect circle to a rather haphazard skyline (e.g., in viscose rayon staple). Some characteristic cross sections are given in Figure 4.

The Surface Structure

The geometrical surface of a fiber may exhibit various types of asperities; in wool fibers it is the scales which protrude from the surface; in man-made fibers it may be crenulations on the surface caused by pigment or dye particles or holes due to the evaporation of volatile components during drying. These macroscopical surface elements are of great importance in spinning. No distinct limit can be specified for these surface-structure effects. The more powerful the optical (or electron) equipment which is used, the more surface details may be distinguished. As a first approximation we prefer to limit the surface structure as far as importance during spinning is concerned to those elements which can be seen under an ordinary microscope at a 400 times enlargement.

The Surface Layer

Wherever materials rub along each other it is known that small amounts of lubricating agents are of decisive importance. In the processing of fibers, where the interfiber surface is of a very considerable size and the interfiber movements during drafting imply large rubbing areas, the importance of lubricating substances in the surface layer cannot be overestimated. Actually, not only are added lubricating agents of importance, but probably the molecular constitution of the fiber substance in the boundary layers also contributes towards the frictional forces during processing.

The processing qualities of natural fibers are to a considerable degree determined by their natural lubricating agents—waxes in cotton, grease in wool, sericine in natural silk; in man-made fibers the correct choice of the type and amount of lubricating agents may be of decisive importance. The choice of lubricating agents for natural fibers too is of great importance when the fiber has been stock-dyed and has thus been robbed of its original "finish." The constitution of the surface layer also may control the generation of static electricity, an effect which may be detrimental in processing.

The Inside of the Fiber

A fiber which due to its "inside" (the material of which the fiber itself is composed) is too weak or too brittle or too stiff cannot be processed on spinning equipment. The inside is also responsible for the behavior of a fiber towards humidity.

The inside of a fiber is responsible for most of the properties of the final cloth which is made from the fiber. Durability, abrasion resistance, tenacity, bending and torsional rigidity, melting point, crease resistance, dye take-up, washfastness, lightfastness, and many other properties are governed by the substance the fiber is built of. For *processing*, however, form and surface layer of the fiber are of more importance than its chemical composition.

The Essential Elements of Spinning Systems

The first step in the conversion of fibers from the bulk form into the carefully arranged one-dimensional form of a yarn is the conversion of the original quasi-at-random situation of the fiber into a sliver; for this process the fiber has to go through cleaning-lapmaking-carding operations which culminate in the typical hardly oriented assemblage of fibers indicated as a "card sliver."

The second series of operations consists of the consecutive attenuations of this sliver through the various slubbing, roving, or gilling-combing, pin-drafting, etc. operations until the final operation on the spinning frame, where the result of all the preceding operations is stabilized by the introduction of sufficient twist into the yarn thus being born.

The differences among the various spinning systems mainly consist in the number of steps in which the attenuation of the sliver is realized, including the number of doublings, and the position and amount of twist which is introduced during this attenuation in order to guarantee sufficient coherence during processing.

Another factor which bears upon the way in which the attenuation takes place in the various spinning systems depending on the length of the fibers is the absence or presence of supporting elements in the drafting field of drawing-, slubbing-, roving-frames or gill boxes etc. in the form of needle-bars or porcupine cylinders. In the processing of short fibers (up to 50 or 60 mm.) the presence of needle bars is not necessary. For fibers from 60 to 70 mm. and larger they are essential.

The two main steps in spinning differ in that during the formation of the sliver there is little or no shearing motion of the fibers relative to each other, whereas the second step is almost completely governed by the interfiber frictional effects which take place during drafting.

It may be useful to notice the order of magnitude of the "thickness" of the assemblages of fibers which are handled in the two main steps of processing. In the cotton system the bulk fiber is first converted into a lap which has a weight of about 500 ktex (500 g./m.; at a width of 100 cm.). After being carded, a sliver weighs about 5 ktex (5 g./m.). The card sliver of the worsted system may be slightly heavier; about 15 ktex (15 g./m.).

After all the drafting operations, yarns result of a thickness somewhere between 10 tex (Ne_1 60) and 100 tex (Ne_1 6).

When one includes all the doubling operations which are introduced between the sliver and the final yarn, an attenuation of about 20–50,000 times has been realized throughout the complete spinning procedure.

This applies for the cotton system. On the worsted spinning system, the total attenuation may be 10 or 100 times larger.

The Characterization of the Processing of Fibers

It is not sufficient to make a visual inspection of a yarn and draw a conclusion on the behavior during processing on the grounds of the quality of this yarn; even a slight extension of the yarn inspection towards quantitative determination of thickness (Nr); twist; strength; elongation; and the evenness of thickness, of strength, and of twist is not sufficient to satisfy the producer of fibers; what he wants is an indication of the type and the seriousness of possible deviations in the behavior of fibers during processing. This task is not an easy one, since many factors apart from the properties of the fiber may contribute to the behavior of a given fiber during processing. There may be differences in degree of opening of the fibers, in the moisture content of the atmosphere and/or of the fiber, in the general condition of the machines (e.g., the sharpness of card clothing), in the setting of the machines, the type of card clothing used, condition of rollers and/or aprons in drafting, the choice of the spinning plan, and a number of other technical factors. Finally, there is the human element; it is known that the skill of the operators contributes to the final quality of yarns.

This means that the same lot of fibers processed on different machinery in different localities may lead to differences in behavior and therefore different appreciation. In general, however, whenever the processing of a fiber does not give satisfaction this will be accompanied by the appearance of breaks, which may occur either in slivers, slubbings, rovings, or yarns. The next undesired phenomenon is the appearance of irregularities—usually in the thickness—in the intermediate or final products of the spinning operations. For the carding can be added the phenomenon of faults in the fleece and in the loading of the card clothing; for the final yarn or intermediate products, e.g., in combed tops, the appearance of neps or slubs, the drawframe may exhibit blocking of the coilers. Finally, during drafting and spinning, fibers may tend to stick (or lick) to cylinders; this is a serious fault.

If asked when he considered the processing of a fiber satisfactory, a spinner might reply "If I can spin Ne_1 80 yarns from 1½-den. staple with less than 20 ends down per 1000 spindle hours and with a lea count product of 1800, I consider it as satisfactory."

For a worsted spinning mill the answer would probably sound considerably different. The number of ends down on a worsted-type ring spinning frame might be 50 or 100 per 1000 spindle hours before the fiber is looked upon as hopeless. In practice it is always found that the variability of the complete equipment used for the conversion of a fiber to a yarn is so great that when a portion of say 1000 kg. of one particular lot is spun today and exactly the same procedure with a second portion of 1000 kg. is repeated two or three weeks later with exactly the same equipment with exactly the same settings, speeds, in the same locality, and by the same people, considerable differences may be observed; see Table I.

TABLE I. Criteria for the Characterization of Behavior During Processing of Fibers on the Cotton System

Processing:
Total waste on the card; composed of flatwaste, cylinder waste, doffer waste, and screen waste
Number of breaks; on slubbing, intermediate, roving, and ring spinning frame
Intermediate products:
Percentage extracted matter
Sliver strength; usually of card sliver and/or draw-frame sliver
Yarns:*
Count (linear density)
Twist
Lea strength and lea × count product
Single-end strength
Single-end elongation at break
Evenness of yarn (U_n 20 m. and U_t 250 m.)
Visual inspection on seriplane:
Inspection of neps, slubs, hairiness, regularity

* Mean value from 15 determinations for each property will in general be sufficient.

For a number of years we have practiced such a check on the spinning properties of our regular rayon staple fiber Td 1.5/38 mm. Once in two years a lot of about 2000 kg. in 10 bales used to be taken from the regular production and stored. Each month a lot of 100 kg. (10 kg. from each bale) was taken and processed to yarn 20 tex (Ne_1 30) and 10 tex (Ne_1 60). During this spinning procedure all the characteristic data mentioned in Table I were assembled and put into graphs.

The "standard spinning procedure" outlined in Table I has been repeated over 75 times through about 7 years. A small section of some of the data thus assembled has been reproduced in Figure 5a and Figure 5b.

In the same way an analogous procedure was followed for the worsted spinning system. Here rayon staple Td 3.75/100 mm. has been processed in quan-

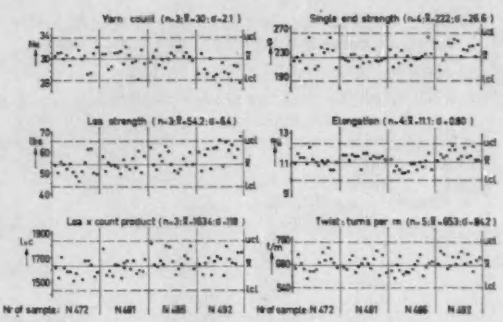

Fig. 5a. Standard spinning procedure of rayon staple fiber Td 1.5/40 mm. for yarn number N$_e$30. Number of cops per sample: $k = 15$. Number of tests per cop: n. Each dot represents the average per cop of n tests.

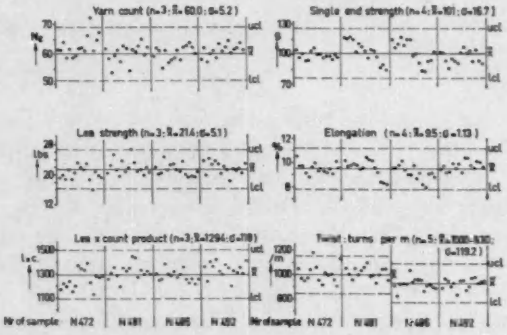

Fig. 5b. Standard spinning procedure for rayon staple fiber Td 1.5/40 mm. for yarn number N$_e$ 60. Number of cops per sample: $k = 15$. Number of tests per cop: n. Each dot represents the average per cop of n tests.

tities of 100 kg. The yarns thus spun were Nm 40. This has been repeated about 16 times through 1½ yr.

These standard spinning procedures supplied the data which served as a background for the evaluation of all the incidental experiments carried through on the cotton and worsted spinning systems. The processing equipment mentioned here consisted of a small though complete set of machines for cotton-system spinning, both for 40- and 60-mm. staple lengths. The worsted system spinning equipment consisted of machinery containing a roller carding engine, a flat combing machine, intersecting, drafting according to the French system (containing no twist), and fine-spinning frames. The number of spinning positions in both departments amounted to about 200 spindles.

The information on processing qualities of lots of staple fiber of about 50 kg. available from such pilot plant equipment should never be considered as more than a first screening. Satisfactory processing on such a scale should never be automatically interpreted into identical behavior in an actual production mill of 20,000–50,000-spindle capacity.

The Algemene Kunstzijde Unie also has, besides the pilot plant research spinning facilities mentioned above, a cotton system spinning mill of about 12,000 spindles [1] and a combing department for making tops with a production capacity of roughly 20,000 kg. a week. By systematic comparison of the behavior of fibers in the pilot plant equipment and the production scale, valuable information has been gained on

TABLE II. General Appreciation of Data Assembled During Processing of Lots of Fiber of 50–100 kg.* Rayon Staple Td 1.5/38 mm.

		Overall appreciation of processing		
		Quite good	Reasonable	Poor (not to be processed on commercial scale)
Total waste on the card (ordinary clothing)		<2%	2–4%	>4%
Ends down on ring spinning frame		0–20	20–40	>50
Lea × count product	Ne 30	1850–2000	1700–1850	<1700
Lea × count product	Ne 60	1350–1500	1200–1350	<1200
Single end strength; g./tex. (= km.)				
	Ne 30	12–13	10–12	<10
	Ne 60	10–11	9–10	<9
Elongation at break		9–12%		<9
Evenness	U_n 20 m.			
(on Zellweger-Uster tester)	Ne 30	10–12	12–14	>14
	Ne 60	12–14	14–16	>16
	U_i 250 m.			
	Ne 30 and Ne 60	1.5–2.5	2.5–3.5	>4

* These data should be considered only as a rough guide for appreciation of the processing of an ordinary rayon staple fiber.

what can and cannot be expected from pilot plant processing information. As a very condensed guidance, some data have been collected in Table II mentioning the minimum requirements for fibers on the cotton system and the worsted system as far as some of the criteria mentioned above are concerned.

Individual Fiber Properties

Whenever fiber properties are mentioned quantitative data should be available for discussion; therefore measuring methods are required.

Length of Fibers

For man-made staple fibers, the measurement of the length of individual fibers (not of bunches of fibers) is in general preferred for both long and short fibers. For the characterization of a staple fiber, measurement of 300 individual fibers is sufficient.

A description of the method in the form in which we usually apply it has been given elsewhere [2]. We will give only a picture of the rulers which have been developed for this purpose (Figure 6). A "crenel" shaped incision, which eliminates incertitude whether a fiber belongs to one class or the next, is used for separating the various classes. For the shortest fibers in a sample, the classes have been combined, thus avoiding precision where it is not essential.

For the exact characterization of fiber length, these rulers have proved their usefulness. If a staple fiber is sold as, for example, 38 mm., it is our opinion that it should be characterized by a *modal* length of exactly 38 mm.; this principle has not been generally accepted. It may happen that a staple fiber is sold as, say, 60 mm. while the modal length turns out to be 56 mm. because sometimes producers characterize their staple fiber by the length at which it has been cut; shrinkage during processing stages after cutting may lead to a definite shortening. For that reason, the *modal* length should be used for the characterization of man-made staple fibers.

Since the modal length of a staple fiber is decisive for roller settings, this point of identity of nominal length and modal length is worthy of consideration for international standardization in order to avoid misunderstandings.

The method of fiber length measurement should also be standardized, since the differences in measuring methods invariably lead to different values for the length of the same fiber.

As an illustration, Table III gives the values for the *modal* length determined in eight different laboratories on the same sample of staple fiber taken from a delivery marketed with a nominal length of 40 mm.[2]

With cotton-type fibers, fibers longer than the modal length are not desirable, although a few of them may not be catastrophic. The indication of the "technical length" is very practical in this respect; the technical length is that length which contains the limit beyond which 5% of the longest fibers in the staple diagram are situated. This technical length should not differ more than one class from the modal length. In Figure 7 an illustration is given of a lot of staple fiber in which the technical length showed

TABLE III. Modal Length of Two Samples of Rayon Staple Fiber Determined in 8 Laboratories
Sample A, nominal length 40 mm.
Sample B, nominal length 60 mm.

Laboratory	Modal length A, mm.	Coeff. of var., %	Modal length B, mm.	Coeff. of var., %
1	38	3.5	56	5.0
2	36	6.4	54	7.7
3	40	4.1	60	5.6
4	39	3.7	57	5.5
5	38	5.4	57	7.0
6	38	7.3	56	8.0
7	41	9.8	58	14.5
8	40	—	58	—

[2] These values were determined under the auspices of the Technical Committee of BISFA. Details of the results will be published elsewhere later. The participating laboratories were Algemene Kunstzijde Unie N.V., Fabelta, Snia Viscosa S.p.A., Société MISR, Egypt, Société de la Viscose Suisse, Syndicat Français des Textiles Artificiels, Vereinigte Glanzstoff Fabr. A.G., Zellwolle Lenzing A.G. Austria.

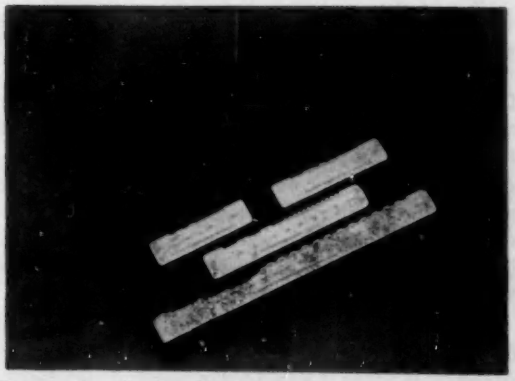

Fig. 6. Set of rulers for the measurement of the length of individual fibers.

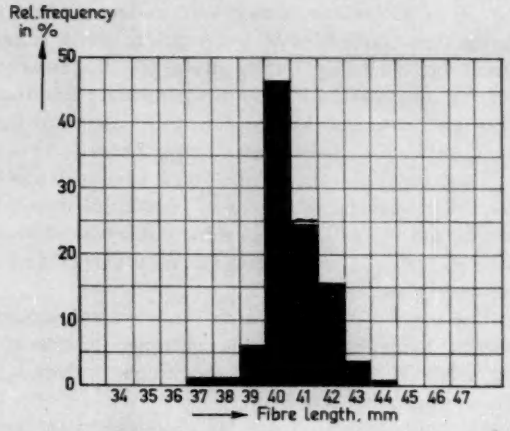

Fig. 7. Frequency distribution of fiber lengths (number of fibers) of a sample rayon staple fiber; Td 1.5/40 mm. Modal length = 40 mm., technical length = 42 mm., mean length = 40.6 mm., coefficient of variation = 2.7%, number of fibers measured = 306.

an undesirable difference of two classes from the modal length. The relation between modal length and roller settings in the cotton spinning system has been described in an earlier paper [3].

It has been found that, for the *worsted system*, blending of fibers with different lengths is to be preferred over spinning of fibers of only one nominal length. For instance, a blend of 80-, 100-, and 120-mm. fibers is in general to be preferred for the worsted system over fibers of only 80 or 100 mm.

Fiber Thickness

For the determination of fiber thickness, or rather linear density of man-made staple fibers, the Vibroscope method, developed by Gonsalves around 1935 [4] is preferred; it has been proposed as a tentative standard method by ASTM [5].

A recent improvement [6] has been developed by Gonsalves which has rendered visual inspection of the vibrating fiber superfluous; the maximum-vibration situation is indicated by an ammeter which indicates a current generated by the vibrating fiber in an electric field in its immediate surrounding. Figure 8 gives a picture of the most recent form of the instrument as used in our research and plant textile laboratories.

Determination of the linear density of individual fibers makes it possible to calculate from measurements of 25 fibers the dispersion in linear density.

In Table IV some data have been assembled indicating the amount of spreading in linear density in samples of various fibers. An appreciation of the variability of linear density of fibers can thus be formulated:

Coefficient of variation, %	6–12	12–18	>18
Appreciation	good	reasonable	unsatisfactory

As to the importance of fiber linear density towards spinning, the spinning limit (finest count) of a fiber is determined by the average linear density. Data have been published earlier in *Rayon Revue* [7].

Fiber Geometry

For the measurement of crimp, several methods are used. The most widely used is the measurement of the number of waves per centimeter of fiber, under carefully controlled conditions [8].

A different method is the measurement of uncrimping energy. In principle this consists of determination of the elongation of an individual fiber at increasing loads and calculation of the energy implied. This gives a value for the "intensity" of the crimp.

By comparing the energy after one partial loading with the same after the fiber has been loaded to much higher tensions, a figure is obtained of the "stability" of crimp [9].

The values for intensity and stability of crimp vary widely in different fibers. In rayon staple the values for the stability of crimp are much lower than in polyamide and polyester fibers.

Cotton-type fibers are invariably characterized by a lower intensity than fibers meant for the worsted

TABLE IV. Coefficient of Variation of the Linear Density of Various Types of Staple Fiber

No.	Sample	Average lin. dens. Td	Coeff. of variation, %
V 271	Viscose rayon	1.56	9.0
V 272	Viscose rayon	2.26	11.4
C 163	Viscose rayon	13.1	13.5
C 150	Viscose rayon	14.3	14.4
C 148	Polyester	1.39	13.4
C 158	Polyester	2.77	21.5
V 278	Polyester	3.40	17.9
V 279	Polyester	3.20	13.9
V 307	Polyamide	1.37	9.6
V 321	Polyamide	1.37	14.4
V 276	Polyamide	1.50	14.8
C 111	Polyamide	4.07	19.4

or woolen system. Table V gives data which characterize some rayon, polyamide, and polyester fibers. Figure 9 illustrates the apparatus developed for these measurements.

The contribution of crimp towards the behavior of fibers during processing is very important, as the following case illustrates.

Two lots of polyamide fiber were processed, the fibers of which were completely identical except that the crimp in the first lot was 6½ waves/cm. and, in the second, 2 waves. The fiber was Td 4.5/110 mm. Although the amount of lubricating agent and the coefficients of friction of both lots were practically identical, it was not possible to process the second one due to a very high number of breaks on the combing machine, the drawing frames, etc.

The difference in behavior is illustrated by the sliver strengths: 68 m. breaking length for the first lot, 19 m. for the second (determined on the combed top).

	U_i (250 m.), %
Evenness of the yarns: lot 1, yarn Nm 40:	6.8
lot 2, yarn Nm 40:	10.2

During the conversion of the crimped man-made fiber into yarn, much of the crimp will be eliminated.

Fig. 8. The vibroscope in its present form as used by the Algemene Kunstzijde Unie.

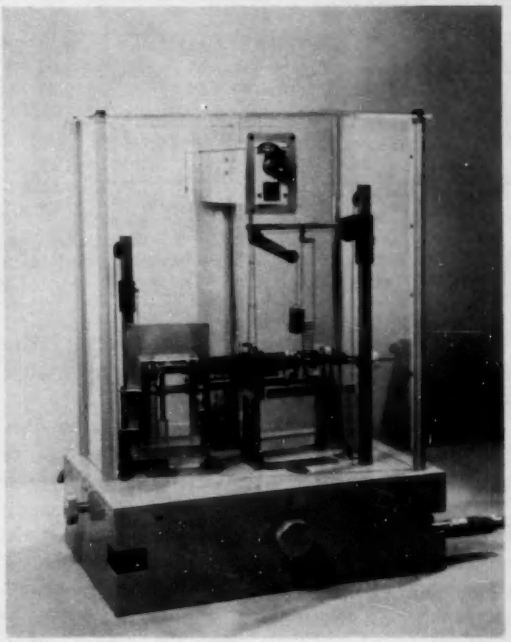

Fig. 9. Apparatus for measuring the intensity and stability of crimp.

TABLE V. Data Characterizing Crimp of Staple Fibers

No.	Sample	Intensity of crimp, mm.×m.	Stability of crimp, %	Crimp ratio
V 217	Viscose rayon Td 2.2/40 mm.	16	26	1.06
C 159	Viscose rayon Td 1.5/38 mm.	20	21	1.07
V 220	Viscose rayon Td 3.75/125 mm.	49	34	1.15
C 162	Viscose rayon Td 13./75 mm.	53	38	1.19
V 276	Polyamide Td 1.5/40 mm.	8	72	1.03
V 241	Polyamide Td 2.75/38 mm.	18	57	1.06
	Polyamide Td 4.5/110 mm.	42	63	1.12
C 113	Polyamide Td 3.0/75 mm.	53	45	1.18
C 115	Polyester Td 3.0/115 mm.	40	67	1.12
V 328	Polyester Td 3.0/100 mm.	56	61	1.16
V 337	Polyester Td 3.75/100 mm.	76	56	1.21
V 341	Polyester Td 3.75/80 mm.	88	60	1.24

TABLE VI. Effect of Processing Upon Crimp of Fibers

Sample	Crimp	
	Intensity, mm. × m.	Ratio
Td 3.75/120 mm. Enkalon staple		
O*	38	1.10
S	20	1.05
W	29	1.08
Td 3.75/120 mm. Perlon staple		
O	38	1.10
S	25	1.07
W	32	1.09
Td 3.0/100 mm. Terlenka staple		
O	64	1.19
S	15	1.05
W	27	1.08

* O = original fibers before spinning; S = fibers taken from the spun and twisted yarn; W = fibers taken from the twisted yarn after a washing treatment.

This is demonstrated by determination of the crimp in fibers before spinning and in fibers taken from a spun yarn (Table VI).

Important, however, is the capacity of the fiber after its conversion into a yarn to recover part of its crimped structure after a relaxation treatment (i.e., after scouring and/or heating). It is this capacity of the fiber to recover partly its crimped structure, however much hampered the fiber may be to respond to this tendency due to the yarn and fabric construction, which will determine the properties of yarns and/or cloth or knitted structure made from them.

Cross section and surface structure are really helpful in processing. The natural fibers are in this respect superior to the man-made ones. Both cotton and wool possess powerful structural elements which facilitate processing. The circular synthetic fibers like polyamides and polyesters are really poorly endowed in this respect. Rayon is considerably better, owing to its lobed cross section. In general it can be stated that in man-made fibers any increase in surface and/or cross section structures can be welcomed as an improvement for the behavior during processing.

The Surface Layer

How the surface layer affects interfiber friction. For the determination of the amount of lubricating substance present in a staple fiber, extraction is the usual technique.

The different types of fiber require different amounts of lubricating agent. For cotton type staple, the amount should remain below 0.60%, preferably even below 0.40%. Higher amounts lead to filling of the card clothing and/or clinging of the fibers to cylinders during drawing.

For the worsted system, higher amounts (up to 1 or 2%) are allowed. For the woolen system, even higher amounts may be permitted.

For the appreciation of the effect of a lubrication agent, we developed a technique [10] which consists of the determination of the static and dynamic coefficients of friction of one fiber rubbing over a cylinder on which fibers of the same sample have been arranged. The apparatus is shown in Figure 10. In Figure 11 the various stages of the preparation of the cylinders are illustrated.

This technique was developed some seven years ago in the investigation of finishing agents in their behavior toward rayon staple fiber. For that application the method is very helpful and reliable. In later years we applied the method to polyamide and polyester fibers; on one occasion we were able to witness some experimental work carried out along these lines on cotton fibers. In Figure 12 a graph has been drawn of the region of the coefficients of friction of rayon, polyamide, and polyester fibers which can be processed in a normal way on the cotton system. Along the abscissa the coefficient of dynamic friction (μ_{pd}) has been plotted and along the ordinate the coefficient of static friction (μ_{ps}). The first characteristic aspect is that in all these cases the coefficient of static friction is higher than the coefficient of dynamic friction. The polyamide staple has an average level of frictional resistance, with the rayon fibers a somewhat lower and the polyester fibers a somewhat higher level. We have found that whenever a lubricating agent was chosen that did bring the coefficients of friction below the dotted line (i.e., a value of the coefficient of static friction lower than the dynamic friction), carding of the staple could not be carried through. The doffer and the cylinder filled and the fleece had insufficient coherence for normal processing. The three man-made staple fibers have one factor in common—a rather poor geometrical surface sturcture.

It is interesting to see the behavior of cotton. In Figure 13 the position of raw cotton and of bleached cotton has been indicated. It is noticed that with ordinary cotton the coefficient of static friction is

well below the coefficient of dynamic friction. The elimination of most of the surface layer, as is the case in bleached cotton, has induced an increase in the coefficient of static friction.

The different constellation of the coefficients of friction of cotton compared with man-made staple fibers must be due to the very considerable surface structure of the cotton fibers. We can only explain the relative high coefficient of dynamic friction of cotton as due to the ribbon-shaped convoluted fiber structure.

In the "naked" bleached cotton fiber this leads to an additional high coefficient of static friction which is decreased in the ordinary cotton fiber by the presence of 0.4–0.6% waxes. If lubricating agents which are known to increase or to decrease the frictional effects of rayon staple fiber are applied to bleached cotton fibers, the result is identical to

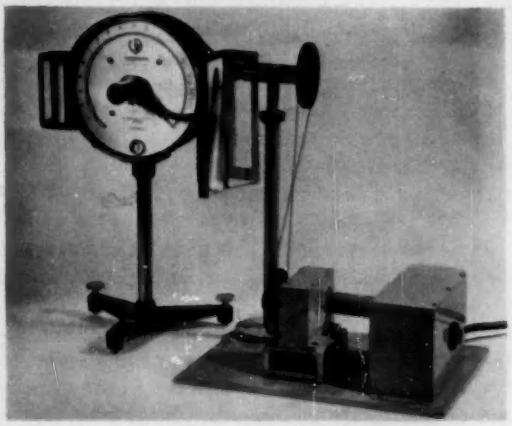

Fig. 10. The apparatus for the determination of the friction of fibers.

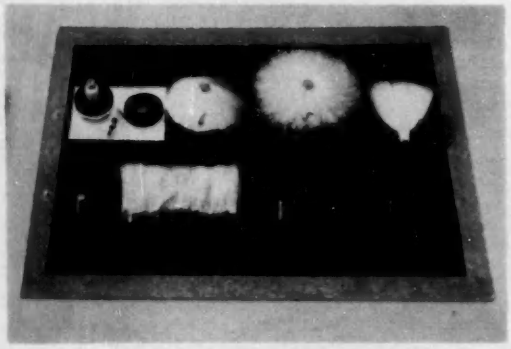

Fig. 11. The various stages of preparation of a cylinder for the determination of coefficients of friction. Counterclockwise from lower right, 1: piece of adhesive tape, 2: tuft of fibers arranged on the adhesive tape, 3: small cork, 4: the adhesive tape rolled around the cork, 5: tuft placed on top of the cylinder and fibers carefully combed, 6: same, 7: ring is shaped over the fibers, thus fastening and straightening them.

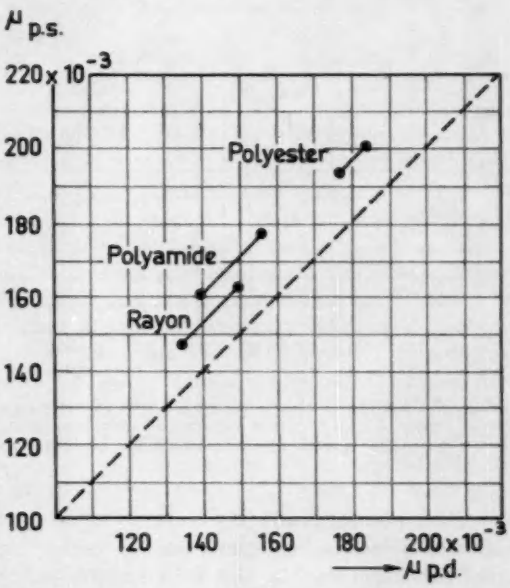

Fig. 12. Areas of the coefficients of friction of various fibers (at 1000-mg. load).

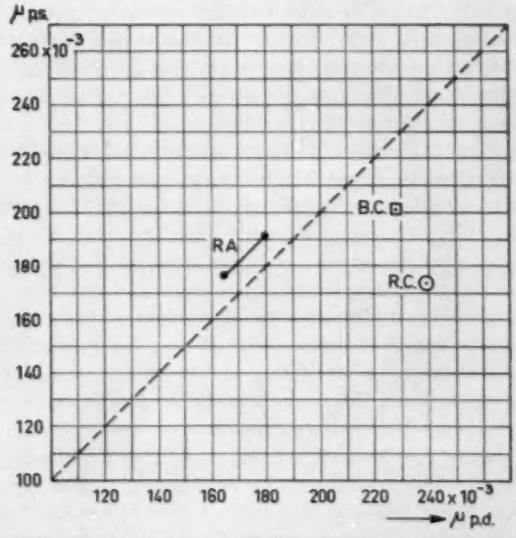

Fig. 13. Coefficients of friction of cotton compared with rayon (at 40-mg. load); RA = rayon, B.C. = bleached cotton, R.C. = raw cotton.

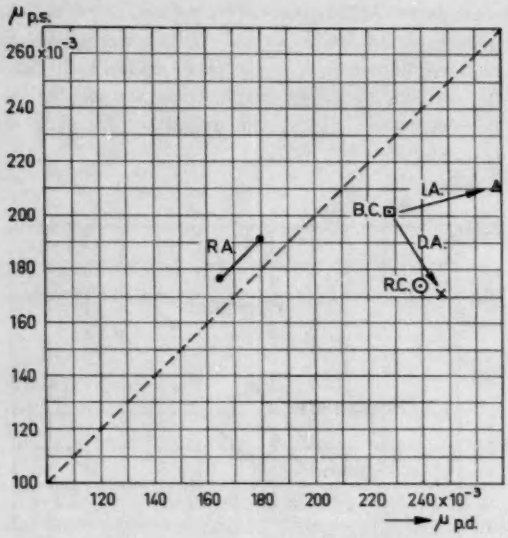

Fig. 14. Effect of finishing agents on bleached cotton (at 40-mg. load); I.A. = frictional resistance increasing agents, D.A. = decreasing agents, other abbreviations as in Figure 13.

their effect with man-made staple fibers (Figure 14). The friction-decreasing agents almost exclusively affect the static friction; this is analogous to the effect of cotton waxes, since the point marked D.A. practically coincides with raw cotton.

It is also identical to the effect of these agents on rayon staple fiber; most of the agents used were of the cationactive type, and on rayon staple these substances are known to give a considerable decrease of the coefficient of static friction.

Cotton fibers with a static friction well below the coefficient of dynamic friction, in contrast to man-made staples, can be processed on the card without difficulty; this must be due to the geometrical surface structure of cotton. The measurement of the coefficients of friction of staple fibers may give useful information on the situation at the fiber surface. For this reason it is particularly suitable for evaluation of the effects of lubricating agents on a chosen type of staple fiber. Since the total effect of a lubricating agent on a fiber surface depends upon the interaction of agent and surface, the same agent may yield different effects on different types of fibers. It has been found, for example, that cationactive agents have a very marked effect on rayon staple fiber, resulting in a considerable decrease of static friction. This effect is absent on application of the same agent on polyamide fibers. The reverse applies to anionic agents.

For rayon staple, systematic investigations carried through earlier [10] have led to the following conclusions concerning the relation between the nature of lubricating agents and interfiber frictional effects:

1. Lubricating agents may affect interfiber friction in a characteristic way.

2. The following general observations have been made concerning the relation between chemical constitution of agents and their affect on interfiber friction:

a. The longer the hydrocarbon chain in the molecule the lower the coefficients of friction.
b. The higher the amount of ethylene oxide groups in the molecule the higher the coefficients of friction.
c. Amide and amine groups decrease the coefficient of friction.
d. A double bond increases the coefficient of friction.
e. Nonionic agents lead to a coefficient of static friction which is greater than the coefficient of dynamic friction.
f. Cationactive agents lead to a considerable decrease of the coefficient of static friction in such a degree that the coefficient of static friction obtains a value which is lower than that of the coefficient of dynamic friction.
g. Anionactive agents affect the coefficients of friction in a degree which is intermediate between the effects of nonionic and cationic active agents.

3. Increase of the amount of lubricating agent over about 0.4% on the fiber gives rise to an increase of the coefficients of friction.

4. Increase of normal pressure leads to a decrease of the coefficients of friction.

5. Increase of interfiber frictional speed increases the coefficient of dynamic friction.

6. Increase of humidity content of fibers affects the coefficient of friction; in general a marked increase of the coefficient of friction occurs when the fibers are in equilibrium with an atmosphere having a relative humidity exceeding 75%.

7. Scroop occurs in rayon staple fiber when the coefficient of static friction exceeds the coefficient of dynamic friction by a certain amount.

8. If the coefficient of static friction exceeds the coefficient of dynamic friction, processing on the

flat card is in general possible. The larger the difference between coefficient of static and dynamic friction the better the fiber can be processed on the card.

9. If the coefficient of static friction is lower than the coefficient of dynamic friction, opening and carding of rayon staple is difficult or impossible.

10. On application of a lubricating agent, based on a suitable oil, on a nonlubricated rayon staple, a decrease of the frictional resistance results. This effect reaches a maximum at an amount of 0.2–0.4% of the agent on the fiber. At quantities higher than 0.6–0.8%, the fiber sticks to cylinders in the drafting field.

11. The finer a fiber, the higher the amount of lubricating agent is required for satisfactory processing. A crimped fiber requires a more effective lubricating agent than a noncrimped one.

How the surface layer affects static electricity on the fibers. The generation of static electricity is a nasty phenomenon; it occurs particularly with the hydrophobic fibers, although it is equally known even with rayon staple if processed under very dry conditions.

However, the surface layer of the fiber may assist in killing static. For that purpose, agents are applied which give rise to an increase in conductivity of the fiber surface, thus eliminating the charges. Cationactive substances and ethylene oxide products are particularly useful in this respect.

However, a fiber which gives no static electricity whatever at a certain moment may give very serious trouble a few months later; a sort of "aging" effect occurs due to the fact that the antistatic agents may diffuse or penetrate from the surface into the fiber and thus lose their beneficial affect upon conductivity (which is always a surface effect). For obtaining sufficient permanence, an antistatic agent should be of such a nature that it does not sink into the particular fiber on which it is applied.

Several instruments and methods are available for measuring the amount of static electricity generated in a fiber upon rubbing [11].

Under the atmospheric conditions of processing, no static should be generated on rubbing the fiber on a foreign surface (i.e., a piece of rubber or a simple comb).

Measurement of static charges by some direct-indicating instrument during processing (e.g., on the card or during drafting) may be very helpful for obtaining quantitative indications. No absolute data can be given here since they vary strongly with the type of instrument used and its location during the measurement.

The Inside of the Fiber

One of the important properties of the "inside" of the fiber is its elastic character (i.e., its response to loads as expressed by its modulus and its strength). In addition, the bending stiffness may be of some importance. Since the inside structure of a fiber simultaneously determines other properties (e.g., torsional rigidity), this property may indirectly also affect behavior during spinning.

The situation is by no means, however, so simple that the stronger a fiber is, the easier it should be convertible into a yarn. A very weak fiber, of course, may soon break in processing and thus thwart spinning; a very strong fiber, however, may refuse to break, dragging along other fibers on stray courses and in doing so equally disturb regular spinning. Since man-made fibers are usually developed with emphasis on strength, the ones which survive the research and development laboratories will seldom fail in this respect; whenever they have a strength over 1.5 g./den. at an elongation at break somewhere between 12 and 60%, spinning will be possible.

Polyamide fibers are characterized by the fact that they have the lowest flexural rigidity presently known. An apparatus for measuring flexural rigidity has been developed in our laboratory [12]. So far this method is applicable only to uncrimped fibers and/or to single filaments of a filament yarn. In Table VII some data are shown which illustrate the flexural rigidity of various fibers. Since sizing and

TABLE VII. Specific Flexural Rigidity of Various Man-Made Fibers (After Scouring); Data Determined on Continuous Filament Yarns

Type	Spec. flex. rigidity, in 10^{-6} g. cm.^{2}
Polyamides	2.5
Acetate	3.5
Viscose rayon N.T.	4.5–5.0
Viscose rayon H.T.	6.0–7.0
Dacron*	7.0
Orlon*	15
Vinyon	15
Cupra (Bemberg rayon)	20–35
Natural silk	16

* DuPont trademark.

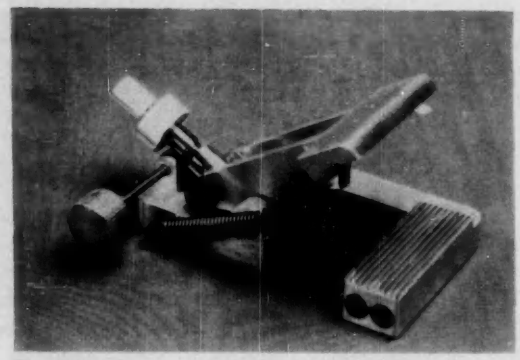

Fig. 15. The upper clamp for the determination of sliver strength, opened.

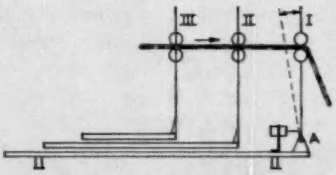

Fig. 16. Principle of the measurement of drafting forces.

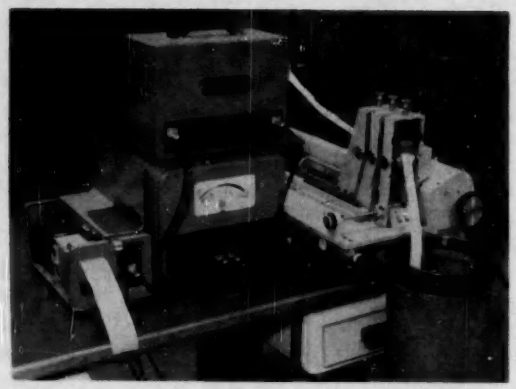

Fig. 17. The apparatus for measuring drafting forces.

TABLE VIII. Sliver Strength for Various Fibers

Rayon staple	7–15 m.
Polyamide staple	4– 8 m.
Polyester	5–20 m.

other agents may seriously affect the flexural rigidity, these data have been determined for carefully scoured fibers. The values have been expressed for fibers of 1 den. (i.e., as a specific flexural rigidity).

Properties of Assemblages of Fibers

Although knowledge of the properties of individual fibers may be useful in studying their behavior during processing, it is not sufficient. During the various spinning operations the fibers interact, and without some quantitative measurements of the result of these interactions, behavior cannot be adequately foretold. We will describe three test methods which may give some quantitative information on the behavior of assemblages of fibers: determination of the sliver strength, determination of drafting-forces, mainly of slivers and rovings of the cotton system, and a relative evaluation of drafting forces in the worsted spinning system.

The Sliver Strength

When an ordinary pendulum tester or any instrument for the determination of the stress–strain diagram of yarns is provided with special clamps to hold a sliver, breaking strength of the sliver can be determined. The shape of the clamps which we developed for this purpose is illustrated in Figure 15.

If a diagram of load versus elongation is registered, very interesting information may be gained from the shape of the curve, in particular the presence (or absence) of stick-slip effects ([10], Figure 8). Introduction of a weak twist, e.g., one or two turns per 20 cm. of sliver, will considerably intensify the appearance of stick-slip effects if these are present. By means of the sliver strength, the amount of coherence in slivers or rovings can be investigated ([13], P91, P92, and P94).

For a general characterization of the sliver strength of various fibers processed on the cotton spinning system, the data of Table VIII may serve. The conditions under which the sliver strength was measured were:

Type of apparatus	: pendulum tester
Specimen length between the clamps	: 50 cm.
Speed lower clamp	: 30 cm/min.
Situation sliver	: untwisted
Expression of results	: in break-meter = 1000 × breaking strength expressed in break-kilometer = $\frac{1000 \times \text{breaking-strength, g.}}{\text{linear density of sliver, tex}}$

The sliver strength is useful as a simple, quick, daily routine control test. On the basis of the knowledge derived from such regular tests, it may be used for obtaining information on the behavior of special lots of fiber.

The Measurement of Drafting Forces

Since drafting forms the essential element in the conversion of fibers into yarns, measurement of the forces generated during drawing of slivers and rovings may supply useful information. For this purpose we developed an instrument which allows precise measurements of these forces under conditions which are identical to drafting on a three-cylinder drawing frame for cotton spinning [14]. The scheme of the instrument is reproduced in Figure 16.

The sliver enters the first drafting field between rollers III and II, driven with a small difference in speed realizing a draft of, for example, 1.25. The main drafting field is between rollers II and I, in which the draft, the cylinder distance, and the roller pressure can be chosen at will. The rollers I are mounted in a frame which pivots at A; the pivoting axis is a torsion bar compensating the drafting force. The very small deviations of the frame due to the drafting forces are picked up by a displacement meter and registered. From the adjustment of the torsion axis and the registered deviations, the exact drafting force can be calculated.

Some characteristic data of the instrument are the following:

Constant speed of delivery	: 6.5 m./min. (By changing the overall drive speed this speed may be changed at will.)
Constant draft in first drafting zone	: 1.25
Draft in main drafting zone	: variable between 1 and 20
Distance of cylinders in drafting zones	: variable between 37 and 250 mm.
Pressure on rollers	: variable between 0 and 10 kg.
Measuring range of drafting forces	: 0–600 g. for the light torsion bar 0–5 kg. for the heavy torsion bar (These forces form the limit of the measuring range of the instrument.)

In Figure 17 a picture of the apparatus is shown.

It was necessary to be able to realize rather small changes in the draft between 1.1 and 2.0; after sufficient gear wheels had been supplied the draft could be increased in 10 steps between 1.06 and 2.0. It was further found that a considerable improvement in evenness of drafting could be brought about by giving the cylinders in the drafting zone a V-shaped tooth profile (see Figure 18).

Drafting forces of card-slivers. The first measurements with this apparatus were made to investigate the effect of drafting on the drawing frame. In Figure 19 an illustration is given of the drafting force versus draft for card slivers of three types of fiber (Figure 19a). In Figures 19b, 19c, and 19d, the behavior of rayon staple and polyamide staple is shown for slivers of a first, a second, and a third passage on the draw frame. The investigated staple fibers were rayon staple, Td 1.5/40 mm., and polyamide staple, Td 1.5/40 mm.

In Figure 20 data are given for two lots of tops of polyester fiber, Td 3.0/80 mm., which differed only in the type of lubricating agent applied.

Certain low drafts lead to relatively high drafting

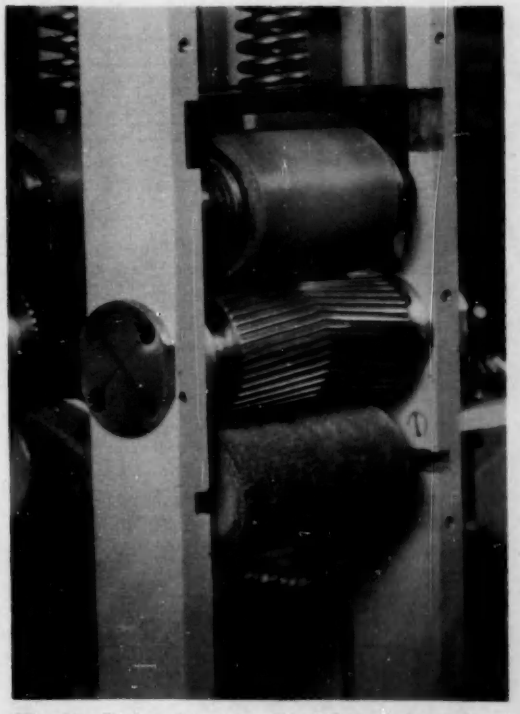

Fig. 18. V-shaped tooth profile of the cylinder surface in the drafting zone of the apparatus for measuring drafting forces.

forces; in other words, in spinning, too low drafts (between 1.2 and 2.0) should be avoided. Similar effects have been described by other authors [15, 16, 17].

This experience has been confirmed in actual spinning practice. A few years ago a paper was published in *Rayon Revue* [18] in which it was pointed out that processing of rayon staple on the spinning frame could be improved by eliminating the top roller of the first drafting zone (instead of a three cylinder drafting field, a two cylinder drafting zone).

More recently it was shown that processing of a blend of polyester and rayon staple on a two line drawing frame (drafting in *one zone*) gives an improvement in regularity of the draw frame sliver in comparison with two-zone drafting. This applies to a sliver in which the fibers have been more or less parallelized by either one combing process or one passage on a draw frame. In Tables IX and X some data are given which confirm this conclusion.

It has been found that the effect of avoiding low drafts is even more beneficial in the processing of polyester and polyamide staple fibers than in rayon staple. The synthetic fibers are in general more difficult to draft than rayon.

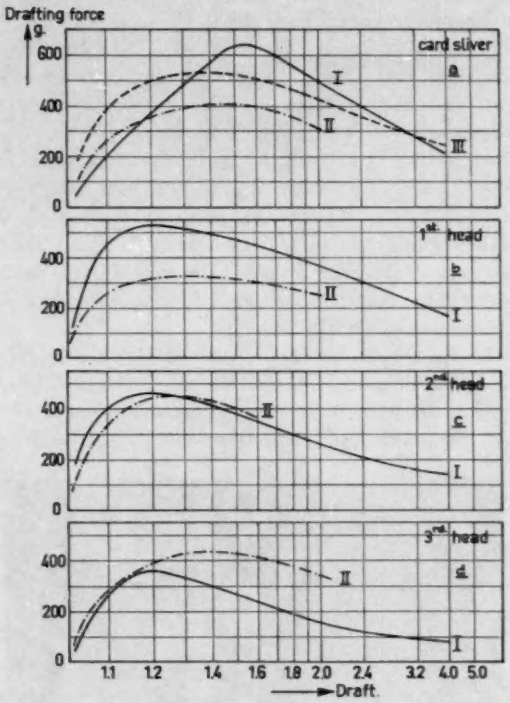

Fig. 19. Drafting forces of various fibers on the drawing frame. I: rayon staple Td 1.5/40 mm., II: polyester staple Td 1.5/40 mm., III: cotton.

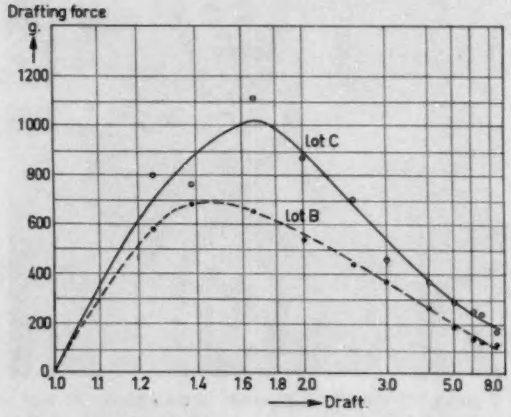

Fig. 20. Drafting forces of two lots of tops of polyamide fibers (B and C); Td 3.0/80 mm.

TABLE IX. The Effect of Two Line Drafting on the Draw Frame

Drawing of rayon staple fiber Td 1.5/40 mm.; the values of the regularity (coeff. of variation) are given.

	Shirley drafting	2 Line drafting
2nd passage sliver	4.4 ± 0.2	3.7 ± 0.2
Finisher drawing sliver	3.7 ± 0.2	3.0 ± 0.2

TABLE X. The Effect of Two Line Drafting on the Draw Frame for Polyamide Fiber Td 1.5/38 mm.; Values of the Regularity (Coefficient of Variation)

	Shirley drafting	2 Line drafting
2nd passage sliver	6.6 ± 0.2	5.8 ± 0.1
Finisher drawing sliver	5.9 ± 0.4	4.6 ± 0.1
Slubbing	9.5 ± 0.6	7.3 ± 0.2
Roving	11.2 ± 0.7	10.0 ± 0.5
Yarn Tex 37 (Ne 16)	17.6 ± 0.6	16.4 ± 0.4
Evenness tested on 250-m. intervals	4.7 ± 0.2	3.6 ± 0.4

TABLE XI. Drafting Force for Enkalon Staple Fiber Roving Ne 2.35 at Draft Ratio 1.1 as a Function of Twist Multiplier

Twist multiplier, α_t	Drafting force, g.
0.40	400
0.45	900
0.50	1200
0.60	1500

Drafting forces of slubbings and rovings. In Figure 21 the drafting force of a slubbing of viscose rayon staple fiber Td 1.5/40 mm. has been drawn as a function of draft.

Figure 22 shows an example of a roving of Enkalon [4] staple fiber Td 1.5/38 mm., twist multiplier $\alpha_e = 0.45$.

In both cases again a relatively high drafting force is found at draft ratios between 1.1 and 1.3, the "dangerous" drafts. In Table XI data which show the effect of increasing twist multiplier are given for the same Enkalon fiber shown in Figure 22.

The effect of twist is further illustrated by the data of Figure 23. In this figure, rovings of a 70/30 blend of polyester fiber with viscose staple fiber with various twists have been compared. To make a comparison possible, the ordinate has been shifted over 10 mm. for each roving. Each curve represents one twist multiplier. Cylinder distance was 44 mm. The drawing force increases upon increase of the twist multiplier.

It had been noticed in the mill that rovings of rayon staple Td 1.2/40 mm. spun on a ring spinning frame often showed slip in the first drawing zone. This same roving was introduced into the measuring instrument in such a way that the first drafting zone was put out of action by taking away the top roller of cylinder III (Figure 16). Drafting was consequently carried out as two line drafting. It was found that on increasing the draft a sharp rise in drafting force was registered (Curve A, Figure 24). At drafts greater than 1.2, however, sometimes the drawing force suddenly dropped to a much lower level (Curve B). At drafts over 1.6, the high-level forces were not found. This means that at drafts between 1.2 and 1.6 two situations may exist: either no drafting occurs at all (Curve A) and consequently the roving slips through the cylinder and the top roller, or ordinary draft takes place (Curve B). Between 1.2 and 1.6 a "dangerous" drafting area exists which in practical spinning should be avoided.

The experiment was repeated with three drafting distances (46, 48, and 50 mm). In each case the same phenomenon was registered.

By measuring the linear density of the slubbing either in the situation A (no drafting) or in situation B (actual drafting), it was found that in situa-

[4] Enkalon is the trade name of polyamide 6 staple fiber (and continuous filament yarn) produced by Algemene Kunstzijde Unie N.V.

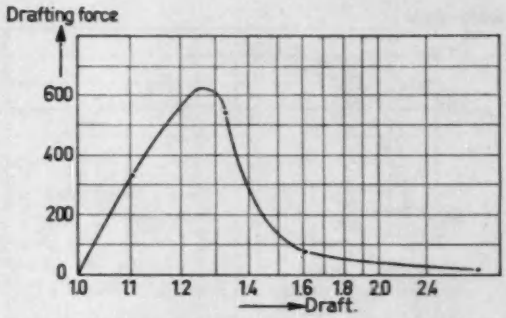

Fig. 21. Drafting force vs. draft of a slubbing N. 0.79 of rayon staple fiber Td 1.5/40 mm.

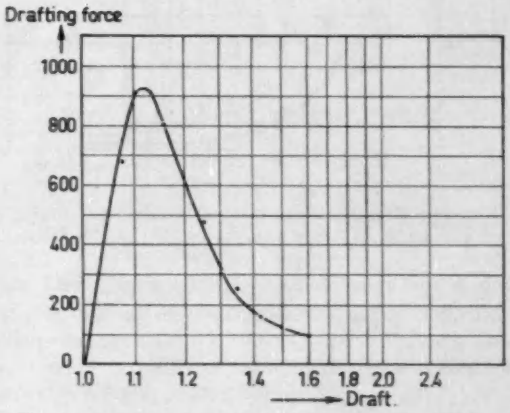

Fig. 22. Drafting force vs. draft in polyamide slubbing of Td 15/38 mm. staple fiber.

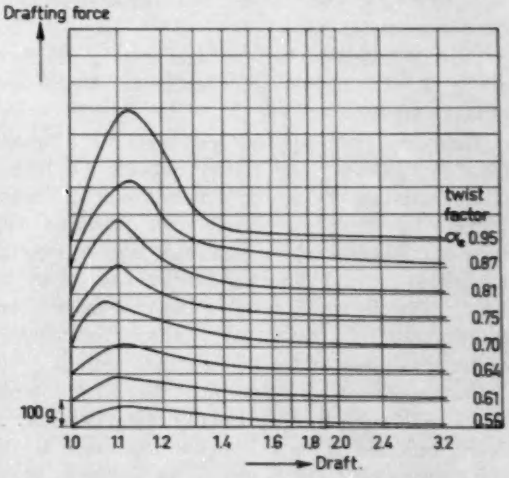

Fig. 23. Demonstration of the effect of twist on drafting force. Rovings of N. 3.27 of 70/30 blend of Terlenka Td 3.0/38 mm. and viscose rayon staple Td 1.5/40 mm.

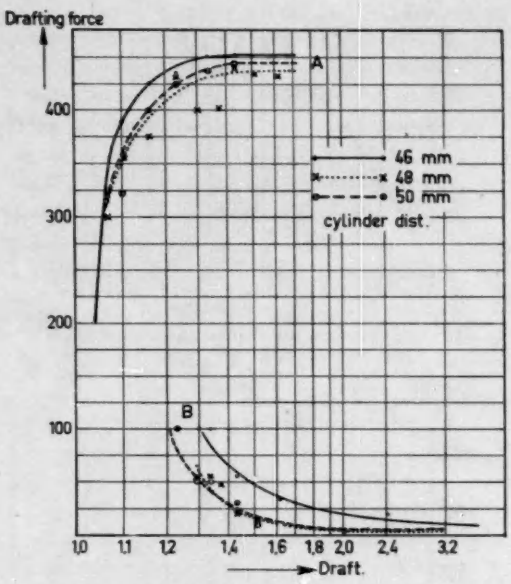

Fig. 24. Drafting forces at small (dangerous) drafts. Rayon staple Td 1.2/40 mm., roving 180 tex (N$_e$ 3.28).

tion A the linear density was the same before and after the drafting zone; this confirms that no drafting took place. Increase of the top-roller pressure did not lead to any change in the situation.

This behavior of man-made fibers is different from that of the natural fibers. The phenomenon of high drafting forces at small draft is found in cotton or wool, but they are considerably smaller than with the man-made fibers.

This is illustrated by the data of Figure 25 in which the drafting forces for slubbings of a number of fibers are shown.

These five slubbings had been spun with "usual" twist multipliers. The cotton slubbing IV, which is characterized by a, for cotton, usual multiplier (which, however, is relatively high compared with twist multipliers used for man-made fibers), exhibits the lowest drawing forces in the area of 1.1 to 1.2 draft. This figure shows that the man-made fibers at relatively low twist may exhibit considerably higher maximum drafting forces than cotton.

Drafting forces caused by the crimp of the fibers. We have found that the amount of crimp in a fiber is clearly reflected in the behavior in drawing. In the first drafting zone a draft of 1.25 was realized; in the second zone the draft was 1.0 (no draft). On introducing various slivers, different "drafting" forces, which we indicate in this case as "contraction forces," were found which clearly correlated with the amount of crimp (see Table XII).

These data clearly demonstrate the important contribution of the geometrical structure to the forces which are generated in drafting.

The instrument for measuring drafting forces in its present form most closely resembles drafting according to the cotton spinning system. This means that there are no needle bars as are usual in the processing of long staple fibers on the worsted spinning system. We have found that the behavior of long staple fibers on the instrument is not in all respects identical to their behavior during actual processing. For example, we came across samples which fiercely resisted drafting (on combing and intersecting frames) but which did not exhibit high drafting forces when measured on the instrument.

Drafting Forces in Long Staple Fibers (Worsted System)

The situation discussed in the previous section has led us to the application of a different technique for evaluation of drafting forces of long staple man-made

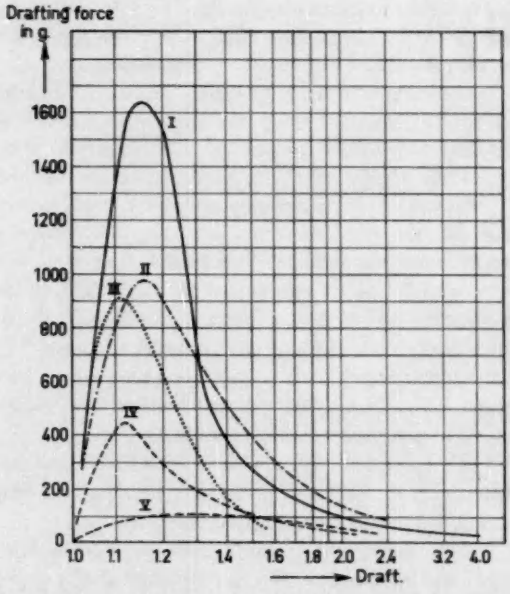

Fig. 25. Comparison of the drafting force vs. draft for slubbings of various fibers. I: rayon staple (twist multiplier $\alpha_e = 0.73$), II: polyester staple ($\alpha_e = 0.63$), III: polyamide staple ($\alpha_e = 0.50$), IV: cotton ($\alpha_e = 0.95$), V: same cotton as IV ($\alpha_e = 0.69$).

fibers. Since, apparently, the presence of needle bars essentially affects the behavior of slivers during drafting, we decided to use an intersecting gill box. The scheme is given in Figure 26.

Four slivers are introduced into the drafting field between cylinders A and C in which they are guided by needle bars. Whenever the drafting forces exceed a certain limit, even after a maximum load has been applied to the toproller C, slip will take place; this is indicated by the fact that toproller C no longer rotates. Using the principle that at a high draft the drafting force is in general low but that it increases upon decrease of the draft, what we actually measure is the lowest draft at which slipping is just avoided (see scheme in Figure 27). The lower the frictional resistance of the fibers, the lower the limiting draft thus found will be.

Of course the number of doublings has to be specified and the load applied to roller C. For the doubling are used either 4 fold or 3 fold (D_4 resp. D_3). For the load are used either 4 weights or 3 weights (W_4 resp. W_3).

Drafts are limited by the number of gears available: we used gears giving drafts between 9.3 and 3.2.

TABLE XII. Drafting Forces—In This Case "Contraction Forces"—At a Draft 1.0 for Various Fibers, and Intensity of Crimp of the Individual Fibers

	Drawing force, g.	Intensity of crimp, mm.×m.
A. Rayon staple Td 1.5/38 mm.	34	21
B. Rayon staple Td 1.5/38 mm., with strong scroop	134	32
C. Polyamide staple Td 1.5/38 mm., crimped	200	50
D. Polyamide staple Td 1.5/38 mm., weak crimp	72	—
E. Cotton, USA, staple length, modus 29.4 mm.	78	—

TABLE XIII. Reproducibility of the Determination of Drafting Behavior on the Intersecting Gill Box; Polyester Fiber Td 3.0/100 mm.

	Lowest draft at which the fiber could be processed; at different adjustments		
Number of doublings (D)	D 4	D 3	D 3
Number of weights (G)	G 4	G 3	G 4
1st measurement	>9.3	6.0	4.9
2nd measurement	>9.3	6.0	4.7
3rd measurement	>9.3	5.7	4.7

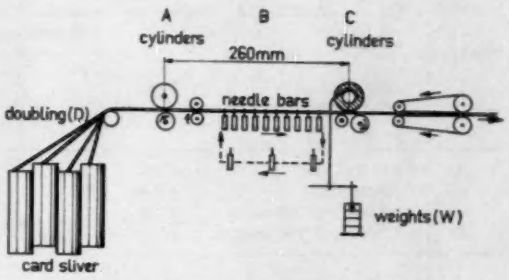

Fig. 26. Scheme of the intersecting gill-box.

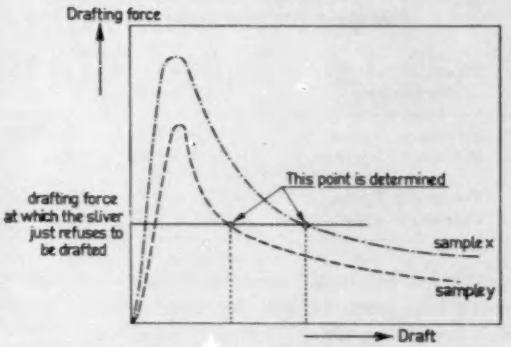

Fig. 27. Principle of determination of drafting force for fibers of the worsted system.

In Table XIII data are given which show that the test is reasonably reproducible.

Recent experiments have confirmed that this type of test gives results which correlate with the behavior during processing. It had been found that polyester staple fiber which had been dyed black gave better results during processing than the same fiber undyed. In addition, processing of 4.5-den. polyester fiber proceeded better than the same fiber in 3.0 den. (all 100 mm.).

Two lots of fiber Td 3.0/100 mm. (one black—A and one white—B) and two lots Td 4.5/100 mm. (one black—C and one white—D) were compared on the intersecting gill box test. The results, given in Table XIV, confirm results observed in practice.

In the processing of long staple fibers, particularly polyamide and polyester fibers, a similar situation holds as has been shown for the cotton-system type of fibers: with long fibers too it has been found of advantage to apply a small number of passages with a relatively high draft rather than many passages with a relatively low draft, as is usual in the processing of wool according to the worsted system.

By reducing the number of passages on the inter-

TABLE XIV. Determination of Drafting Behavior of Four Samples of Polyester Fiber (Intersecting Gill-Box Test)

Adjustment	Color	Lowest draft at which fiber could be processed; for various adjustments							
		D4	G3	D4	G4	D3	G3	D3	G4
A Td 3.0/100 mm.	black			7.9		4.9		4.1	
B Td 3.0/100 mm.	white			9.3		6.4		5.1	
C Td 4.5/80 and 100 mm.	black	5.4		4.7					
D Td 4.5/80 and 100 mm.	white	9.3		7.9					

TABLE XV. Comparison of Spinning Yarns Nm 40 on the Worsted System with Five and with Three Passages on the Intersecting Gill Box

Fiber: Td 4.5/80–100–120 mm.	Evenness	
	U (20 m.) %	U (250 m.) %
Polyester 5 pass.	13.6 ± 0.5	4.0 ± 0.4
Polyester 3 pass.	13.3 ± 0.6	3.2 ± 0.3
Polyamide 5 pass.	17.8 ± 0.7	4.5 ± 0.3
Polyamide 3 pass.	17.4 ± 0.4	4.0 ± 0.2

secting gill box from five to three, the evenness of the yarns thus spun was not decreased. In Table XV data are shown which illustrate this effect.

Recently experiments have been carried out on pure polyamide and polyester fiber as well as on various blends of these fibers with wool and on pure wool to compare the behavior of such fibers towards processing on five and on three intersecting gill box passages. It was interesting to observe that while the pure man-made fibers benefitted from the three-passage system, pure wool gave better results with the five-passage spinning plan. As to the blends, which contained 25, 50, and 75% wool added to respectively 75%, 50%, and 25% polyamide or polyester fiber, here again the five-passage plan gave better yarns than the three-passage plan. Apparently as soon as sufficient wool is present in the blend more steps with lower drafts are preferable over fewer steps with higher draft.

Concluding Remarks

A rough description has been given of the most important characteristics of man-made fibers as far as their behavior during spinning is concerned. Since, in spinning, all the various characteristics of the fibers simultaneously contribute to the behavior during processing, spinning behavior cannot be foretold on the basis of the individual fiber characteristics alone.

For this reason it is more useful—although at the same time more complicated—to collect data of "collective fiber properties," such as the determination of drafting forces.

For the analysis of complex properties like drafting forces, knowledge of the individual fiber properties is very helpful.

By systematic application of the technique of measurement of drafting forces, we hope to be able to further extend and widen our insight into the behavior of fibers of different type and character during processing.

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A Comparison of Three Methods (Single and Double Rip) for the Determination of Tearing Strength of Fabrics[1]

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Abstract

Three essentially similar methods for measuring the tearing strength of fabrics have been examined on a comparative basis. The experimental difficulties arising in the tearing of certain fabrics have been studied with a series of fabrics exhibiting different tearing characteristics. The study has confirmed the advantage claimed for the experimental principle of the "wing-rip" method. The records of tearing force obtained by each method on an inertialess testing machine have been analyzed by the procedures stated in each of the three methods. It is shown that the essential differences among numerical values derived from the three methods are due primarily to differences in the analytical treatment of the data.

It is concluded that all three methods measure the same fabric property. A single new method, comprising a combination of the experimental and analytical procedures now required by different methods is recommended (1) to accommodate the tearing characteristics of a wider range of fabrics, (2) as equally suitable for use with testing machines involving a high degree of mechanical inertia and others of the inertialess type, and (3) to yield a practical maximum of stability in the average values derived.

THE manner in which a fabric tears is governed by a number of factors, some of which arise from its construction. Among these, of course, are the strength of individual yarns, the weave pattern of the cloth, and the firmness with which yarns are held in the fabric. The latter is of particular importance in the measurement of tearing strength by single and double rip methods, in which yarn movement depending largely upon the form of the test specimen may affect the record of tearing force. This characteristic renders it difficult or even impossible to obtain satisfactory numerical values for certain fabrics by these methods, but may constitute a factor of merit in the utility of the material. Obviously the ideal test method should take account of all important factors entering into the service situation and combine these appropriately in arriving at a result highly correlated with field performance. We have not yet arrived at this point so far as the tearing of fabrics is concerned, and in fact may not reasonably expect any single index to reflect all of the complexities of tearing produced by varied and quite different circumstances. Nevertheless, the elimination from test methods of phenomena characteristic of the methods rather than of the materials under test is an overriding principle which remains valid despite practical test method difficulties. The assessment of tearing behavior in descriptive terms might be worth while as an adjunct or as an alternative to the numerical

[1] DRML Report No. 69-2 (PCC No. D49-75-70-05).

index bearing upon performance under the limited conditions of some test methods, whose primary purpose is to obtain a reproducible numerical measure of performance.

Purely as a matter of economy, earlier work [2, 3] comparing the Canadian single-rip method with the trapezoid method on testing machines of different types employed weft tearing only in obtaining the experimental data. In that study all of the fabrics examined behaved well under test. With many of the same fabrics, however, it was subsequently observed that in the application of the CGSB single-rip test to the stronger set of yarns (usually the warp) certain yarns did not rupture but instead were withdrawn from the specimen by the forces applied in the tearing procedure. Frequently, puckering of the fabric also occurred to a greater or lesser extent, accompanied by a translation of yarns, which in some cases amounted to their complete withdrawal. The validity of the results of tests in which yarns have been withdrawn from the test specimen rather than ruptured in proper sequence during the course of the tear is open to question. Although the behavior of the fabric under test reflects fabric properties related to resistance to tearing, yarn translation or movement depends primarily upon the nature of the test specimen employed in the testing procedure. In actual service, evidence of yarn movement is found in the puckering of the fabric close to the tear, but rarely will a yarn be translated without rupture, unless the tear is close to a seam or other cut edge of the fabric.

In the CGSB single-rip method, the effect of yarn withdrawal is generally to increase the force recorded by the testing machine, since the forces involved in the withdrawal are superposed upon those arising from the normal tearing situation located at a point further along the path of the tear. The length of record affected by a single withdrawal is frequently uncertain, since the magnitude of the forces involved depends upon the sequence of events attending the movement of the yarn. Observation of the specimen during tearing or inspection later will usually reveal whether or not yarns have been withdrawn rather than ruptured. Where yarn withdrawal is frequent, it may be impossible to accept any portion of the record as a valid representation of the tearing strength which the test method is intended to measure.

The experimental evidence suggests that more than one mechanism may contribute to the variations in tearing force resulting from yarn withdrawal. Progressively increasing resistance to withdrawal may result from puckering of the fabric along the line of yarn movement. Such a resistance appears in some cases to lead to the rupture of the partially withdrawn yarn, while in other cases sudden partial or complete release of the yarn occurs before the point of rupture is reached. Examples of yarn withdrawal have also been noted, however, in which no puckering took place, although the effect upon the record was characteristic and unmistakable.

Experimental Procedure

The preceding criticism renders the CGBS single-rip test unsatisfactory for use in connection with fabrics in which yarn withdrawal can occur during the test. It is not always possible to distinguish the consequences of yarn slippage or withdrawal and eliminate them from the calculation of the tearing strength value, and indeed there is considerable doubt as to whether such a treatment of the recorded data is desirable or justifiable. In considering this problem, two fairly obvious approaches were recognized. The first was to modify the dimensions of the test specimen, or to change its character, in such a way as to eliminate yarn slippage effects. Efforts in this direction included a study of specimen widths up to 12 in., the incorporation of a hem along either outside edge, and the use of adhesive material along outer edges to prevent yarns from slipping. None of these expedients led to a procedure satisfactory in all respects. Wider specimens tended to allow less yarn slippage but did not eliminate it. Hems were of little or no value whatever. Adhesive impregnated into the edges of test specimens prevented yarn withdrawal, but very severe puckering frequently resulted. This expedient was also considered capable of obscuring characteristics of fabric tearing behavior which it is of interest to observe. These experiments, which involved a range of fabrics of quite dissimilar character, failed to lead to any successful but minor modification of the test specimen as a means of adapting the method to fabrics of irregular tearing behavior.

The second approach was to examine closely related test methods to see whether the problem of yarn withdrawal was a common characteristic. This approach led to the comparison of the L.I.R.A. "Wing-Rip" test (Appendix III) with both the

CGSB single-rip test and the Shirley Institute tongue tear (double-rip) test. In addition to the inquiry into the incidence of yarn movement during tearing, the relationship among values obtained for the same fabrics with these three different methods was of interest. For this investigation a series of 11 fabrics [2] was selected, on the basis of earlier studies with the CGSB single-rip method, to afford examples of regular tearing behavior, yarn withdrawal, and the reversion of tearing to the crosswise direction of the specimen. Sets of test specimens were cut from each fabric in such a manner that the same yarns occupied corresponding positions in the path of the tear in corresponding specimens for each test method. Due to limitations of time and material, five test specimens only were tested by each method for each direction of each fabric. Experimental procedures were precisely as laid down for the three methods, and in the first instance the calculation of tearing strength for each method was also carried out as specified. Subsequently, as described later, the treatment of the record prescribed by one test method was applied to the records of the others with interesting results. The three methods examined were the following, the first two listed being given in detail in Appendices to this paper.

1. CGSB Schedule 4-GP-2, Method 12.1 (26th December, 1957)
2. L.I.R.A. Wing Rip Test, Memo. No. 1119 (9th December, 1955)[3]
3. Tongue Tear Test (Shirley Institute) p. 165, Methods of Test for Textiles, Handbook No. 11, British Standards Institution (1956 edition)

The entire series of tests was carried out on the Instron Tensile Testing Machine, operated in an atmosphere of 65% RH and 70° F. in which test specimens were conditioned prior to testing. The data obtained are summarized in Table I, average

[2] See Appendix I.

[3] See also [1].

TABLE I. Tearing Strength of a Selection of Fabrics by Three Test Methods

Fabric	Warp tearing strength, lb.			Weft tearing strength, lb.		
	Single rip	Wing rip	Tongue	Single rip	Wing rip	Tongue
15-3	3.28	4.08	5.44	2.58	3.38	4.52
19-3	40.0mW (34.4)a	40.6	61.4p	38.3m	41.2	63.2
20-[illegible]	5.53W (4.95)b	5.38	7.74P	R	8.22	11.29wRc
23-[illegible]	5.67W	5.88	10.13W (9.75)wd	5.20wm	6.02	9.13
24-2	2.79	2.98	4.40	2.46	2.98	4.20
25-4	7.80	8.54	13.03	5.66	5.90	9.73
27-2	5.95	7.21	11.05	5.52	6.87	10.06
28-2	3.83w (3.67)d	4.02	5.35p	4.32P	5.05	6.41p
96	8.33wP	7.23	—	6.85wP	6.36	—
97	R (12.50)We	12.02wP	—	12.3w	10.50wP	—
98	5.96W	6.43Pm	—	6.2wP	6.93wPm	—

m—Yarn translation but not complete withdrawal.
p—Specimen showed slight puckering.
P—Severe and general puckering.
R—Tear reverts to crosswise direction of specimen.
w—Yarn withdrawals, but less than three yarns per specimen. In such cases an adequate length of record was available for the calculation of withdrawal-free values for tearing strength.
W—Extensive withdrawal of yarns.
(a)—An average of twenty peak values only from five specimens, taken from portions of the records considered free from yarn movement or withdrawal effects. Each specimen provided three or more of these observations.
(b)—An average of sixteen peak values only from four specimens, as per note (a). Fifth specimen record rejected entirely.
(c)—Reversion of tear in one specimen only (rejected). Value given is derived from three specimens, using portions of record free of yarn movement or withdrawal effects.
(d)—This value calculated from five specimens, using portions of records substantially free of yarn withdrawal effects.
(e)—Calculated from two specimens only, both exhibiting yarn withdrawals whose effects could not be eliminated from the calculation. Other specimens reverted to crosswise tear.

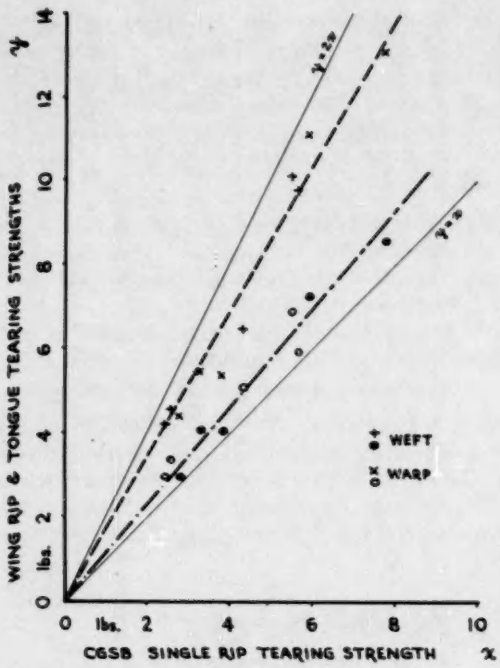

Fig. 1. Comparison of tearing strength values determined by three methods prescribing different experimental and analytical procedures.

values for each set of five specimens being given, in some cases subject to qualifying notations given in the table. In certain instances, made clear in the table, it was necessary to inspect carefully both the tested specimen and the record obtained with it, in order to arrive at a value of tearing strength essentially free from the influence of yarn withdrawal forces. For one or two fabrics this required the discard of the entire record obtained with certain test specimens, and the value given is based upon fewer than the intended number of replicates. With the exception of notes (a), (b), (c), (d), and (e), all values given in the table were calculated from the record of tearing force with no attempt to eliminate effects due to yarn movement and withdrawal or puckering. The majority of the values therefore constitute the results of the application of the test methods as written, without regard for any characteristics of behavior peculiar to the specimen under test. In general, this is considered a fair treatment, excepting cases marked W, in which the values calculated are probably not to be accepted as representing tearing strength in the sense of regular tearing behavior.

It is of interest here to note that whereas the effect of yarn withdrawal is normally to record a tension higher than that of regular tearing, in one rather unusual but significant case the effect may have been the reverse. With the nylon "rip-stop" fabric 98 (of the usual construction), the doubled ends intended to impart the rip-stopping character to this material frequently were withdrawn from the tails of the test specimen without breaking in the CGSB test procedure, and the test almost certainly failed to obtain a measure of the true merit of the fabric. This particular fabric was characterized also by severe puckering, together with minor yarn withdrawal or movement, in both test methods applied to it.

Discussion

Several interesting points arise for discussion in the results obtained above. The differences in behavior of various fabrics are obvious, with ample illustration of the puckering of the test specimen, yarn movement, and yarn withdrawal. It is reasonable to accept puckering and yarn movement within the specimen as concomitants of tearing, since these may properly characterize the fabric. Yarn withdrawal, however, as a characteristic of the test specimen, reflects a deficiency of the test method. Insofar as these effects pertain to the nature and dimensions of the test specimen rather than the fabric under examination, the test results are suspect and may properly be questioned. Many fabrics, of course, are free of irregular behavior, as indeed were four of the group examined here, when tested by any of the known methods.

In comparing the three test methods here examined, the relatively greater tendency of the Canadian single-rip and the double-rip methods to induce complicating effects is clear. In view of the mechanical similarity of these two tests, one would expect them to exhibit the same characteristics in this respect. It has been stated [1] that the wing-rip method was developed as a means of testing fabrics in which tearing tended to revert to the crosswise direction in other methods. Although only two of the fabrics tested here (20-2 and 97) afford evidence on this particular point, it is very apparent that the L.I.R.A. test method enjoys comparative freedom from other complications also. With the exceptions of the drogue fabric 97 (a very open weave material) and the nylon rip-stop fabric 98, none of the materials examined performed irregularly when tested by this

procedure. In the two exceptional cases, severe puckering was observed; while minor yarn withdrawal or movement was also noted, it was possible to eliminate the portions of the record influenced by these effects in calculating the tearing strength of these materials.

The comparison of the numerical values obtained for each fabric by the three methods is of considerable interest. In this connection it is important to note that the methods differ in the derivation of the tearing strength from the tearing force record. The British tongue method requires the determination of the median peak value for each specimen. The CGSB single-rip method averages the single highest peak values from each of ten successive equal portions of the record, representing 2½ in. of tearing. The L.I.R.A. wing-rip method utilizes the single highest maximum only, derived from 1 in. of tearing. In each method the values thus obtained for all specimens tested are averaged. On the basis of these differences in treatment of the data, it would be expected that the wing-rip test should yield higher numerical values than the Canadian single-rip method, and that values obtained by the tongue method should be less than twice those of the single-rip method. The data for the "regular tearing" fabrics of Table I are plotted in Figure 1. The approximate relationships of the test results obtained by the three methods are clear, and support the expectations stated above. Although approximate conversion factors can be derived from Figure 1, their use as a means of calculating test results for any method from test results obtained by another method would be a very dangerous procedure.

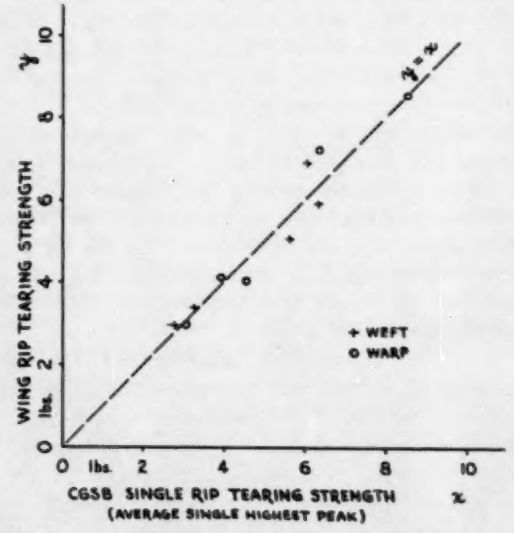

Fig. 2. Comparison of average single highest peak values, from records obtained with the L.I.R.A. wing-rip method and the CGSB single-rip method.

TABLE II. Comparison of Canadian Single-Rip and L.I.R.A. Wing-Rip Test Results Utilizing Single Highest Maximum Force (lb.) Recorded *

Fabric	Wing-rip		Single-rip	
	Warp	Weft	Warp	Weft
15-3	4.08	3.38	3.94	3.28
24-2	2.98	2.98	3.06	2.78
25-4	8.54	5.90	8.55	6.38
27-2	7.21	6.87	6.39	6.09
28-2	4.02	5.05	4.57	5.63

* Treatment of data prescribed by the wing-rip test method.

TABLE III. Comparison of Three Test Procedures by Median Peak Values from Tension Records (lb.) *

Fabric	Tongue tear		Single-rip		Wing-rip	
	Warp	Weft	Warp	Weft	Warp	Weft
15-3	5.44	4.52	2.66	2.08	2.77	2.38
24-2	4.40	4.20	2.50	2.15	2.38	2.26
25-4	13.03	9.73	7.26	5.13	6.98	4.93
27-2	11.05	10.06	5.72	5.28	6.75	5.92
28-2	5.35	6.41	2.97	3.46	2.73	3.21

* Treatment of data prescribed by the tongue test method.

Because of the differences among the three methods in the treatment of the record obtained from the testing machine, the real similarity of the methods is not apparent in Table I or Figure 1. It becomes clear, however, when their records are treated in the same manner. For example, if one utilizes only the single highest maximum in the CGSB single-rip test, the comparison between the results so obtained and those of the wing-rip method appears as in Table II and Figure 2. On the other hand, if the "median" treatment used in the tongue test method is applied to the records of the CGSB single-rip and wing-rip tests, the comparison of Table III is obtained.

In Figure 3 are shown the data of Table III, together with values obtained in an earlier similar but unpublished study of the single-rip and tongue methods, in which the value of the median peak was determined as a basis for comparison. In all three figures lines representing $y = x$ or $y = 2x$ have been drawn,

without regard for the experimental data, as a matter of interest.

From Figures 2 and 3 there can be little doubt that the same property of the fabric is measured by each of the three test methods, and that similar numerical values are obtained with these methods provided that the experimental data are treated in the same manner. In making this generalization it is admitted that differences in the length of the tear represented by the record have been ignored. It must also be noted that the supporting data have been obtained with an inertialess testing machine capable of providing great detail in the record of the tearing force. It has not been established whether the characteristics of other types of testing machines may influence differently the comparison obtained among the three methods considered here, but in view of the basic similarity of the methods it would be surprising if this turned out to be the case. It is clear, nevertheless, that no really good technical evidence exists for the choice of any particular method over the other two of those examined here, except that of test specimen tearing behavior discussed above. On this basis the experimental principle of the wing-rip method deserves careful attention.

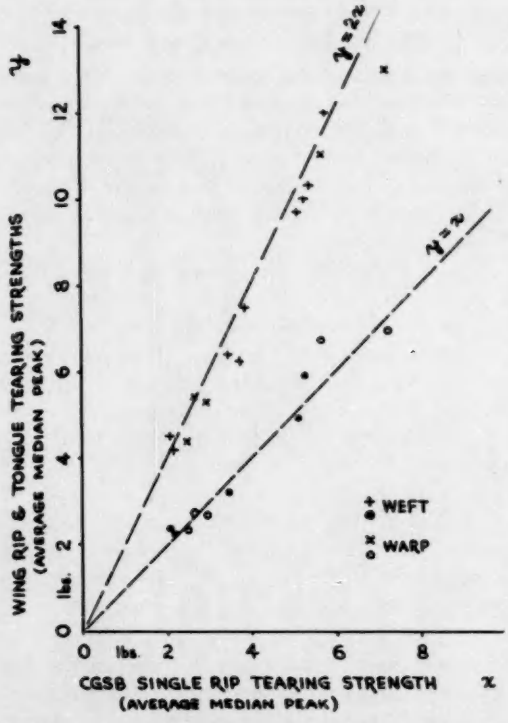

Fig. 3. Comparison of average median values from records obtained with the L.I.R.A. wing-rip, the CGSB single-rip, and the Shirley Institute tongue methods.

The comparison of testing machine types reported earlier [2] demonstrated the influence of machine characteristics upon the tearing force record. Pendulum types of machines involve an inertia factor which is frequently great enough to prevent the recording of many of the fluctuations in tearing force which actually occur in the test specimen but which are recorded when an inertialess testing machine is employed. The procedure by which the numerical tearing strength value of each specimen is derived must therefore accommodate a wide variation in the number and type of peaks appearing in the record, if the method is to apply to all types of testing equipment now commonly in use. The influence of machine inertia, however, cannot be eliminated from the test results, and this basic difference in the quality of the recorded data will be reflected in the derived tearing strength values. Even though the test results may depend upon the type of machine used, it is a matter of practical importance that the test method as a whole be so written as to apply clearly regardless of individual machine type characteristics.

The Canadian revision (December 1957) of the single-rip method attempts to take account of the inertia problem in requiring the use of one maximum value from each of ten successive equal portions of the tearing force record. This requirement specifies a treatment which can readily be applied to records obtained from any type of testing machine, regardless of the detail in which the actual fluctuations of tearing force have been recorded. At the same time considerably greater stability of the mean value is obtained than from the use of a single maximum value from each test specimen. The use of the median peak value, of course, affords the greatest stability, but its merits can be realized only with records of sufficient detail.

In Table IV are given values derived from the same set of records (obtained by the experimental procedure of the CGSB single-rip method on an inertialess testing machine) by the analytical procedures prescribed in the three test methods forming the basis for this study. Five replicate specimens in each direction for five fabrics exhibiting "regular" tearing behavior are represented here; they constituted part of the study leading to Figures 1, 2, and 3.

TABLE IV. Stability of Mean Values for Tearing Strength Calculated from the Same Tearing Force Records by Alternative Analytical Procedures

(Experimental Procedure: CGSB Method 12.1, 1957 Revision)

Fabric	Median peak values[1] Mean, lb.	S. deviation, lb.	S. deviation, %	Average of ten highest peaks[2] Mean, lb.	S. deviation, lb.	S. deviation, %	Average of single highest peaks[3] Mean, lb.	S. deviation, lb.	S. deviation, %
15-3 Warp	2.66	0.19	7.2	3.28	0.30	9.1	3.94	0.26	6.6
15-3 Weft	2.08	0.15	7.2	2.58	0.20	7.8	3.28	0.33	10.0
24-2 Warp	2.50	0.14	5.6	2.79	0.15	5.4	3.06	0.21	6.9
24-2 Weft	2.15	0.10	4.7	2.46	0.09	3.7	2.99	0.14	4.7
25-4 Warp	7.10	0.24	3.4	7.80	0.14	1.8	8.55	0.18	2.1
25-4 Weft	5.13	0.07	1.4	5.71	0.18	3.1	6.38	0.53	8.3
27-2 Warp	5.72	0.22	3.8	5.95	0.17	2.9	6.39	0.21	3.3
27-2 Weft	5.28	0.14	2.7	5.52	0.17	3.1	6.09	0.25	4.1
28-2 Warp	2.97	0.14	4.7	3.67	0.13	3.5	4.57	0.44	9.6
28-2 Weft*	3.46	0.20	5.8	4.32	0.31	7.2	5.63	0.62	11.0
Av'ge value	3.90			4.41			5.09		
Av'ge S. deviation			4.65			4.76			6.66

[1] Required by Shirley Institute tongue test method.
[2] Required by CGSB Method 12.1 (revised 1957).
[3] Required by L.I.R.A. wing-rip test method, but taken here from record of 2½ in. of tearing.
* Puckering of fabric noted.

It will be noted that the stability of the mean value increases, while the mean value itself decreases, as larger numbers of peaks are utilized in computing the tearing strength of the individual specimens. These results are not, of course, unexpected, but deserve consideration in the choice of the analytical procedure by which the final numerical mean value is to be calculated.

Conclusions and Recommendations

It is concluded that all three of the test methods compared in this study measure the same fabric property and yield essentially the same measure of it if the experimental records are treated in the same manner. The experimental procedure of the wing-rip method suffers least from complications arising from the tearing behavior of certain fabrics.

It is suggested that a combination of the experimental principles of the L.I.R.A. wing-rip test procedure and the treatment of the data required by the revised (1957) CGSB single-rip method might result in a more widely useful test method. Such a method might, for example, utilize as a matter of fabric economy a test specimen similar to that of the CGSB method, but require that the tails of the specimen be gripped in the jaws of the testing machine at an angle, after the manner of the wing-rip method. Empirically, the choice of angle appears not to influence the tearing strength value derived, and may not be critical within wide limits. Ewing [1] suggests 55° as an optimum value chosen to serve the widest range of fabrics. These methods have experimental advantages of economy and satisfactory tearing behavior; the analytical treatment of the tearing record should be capable of unequivocal application to records from any of the variety of testing machines now in general service, and should also maximize the stability of the derived tearing strength value. The CGSB revised procedure represents a practical compromise to achieve these objectives.

Author's Note [4]

Since the text of this paper was prepared it has been brought to our attention that some tensile testing machines in common use are not capable of recording tears more than 2 in. in length. The requirement of 10 successive ¼-in. intervals of tear cannot be met with these machines; 10 (or fewer) peak values may, however, be taken from equal intervals totalling not more than the maximum length of tear

[4] This note submitted July 23, 1958.

TABLE V. Mean Tearing Strength Calculated from Peak Values Taken from Five Successive Equal Intervals of Tear Record

(Experimental Procedure: CGSB Method 12.1, 1957 Revision)

Fabric	Average of five highest peaks Mean, lb.	St. deviation, lb.	St. deviation, %
15-3 Warp	3.17	0.24	7.6
15-3 Weft	2.74	0.28	10.2
24-2 Warp	2.63	0.15	5.7
24-2 Weft	2.30	0.07	3.1
25-4 Warp	7.87	0.21	2.7
25-4 Weft	5.77	0.31	5.4
27-2 Warp	6.00	0.17	2.8
27-2 Weft	5.37	0.21	3.9
28-2 Warp	3.68	0.25	6.8
28-2 Weft	4.20	0.38	9.0
Average value	4.37		
Average st. deviation			5.7

recordable. The records forming the basis for Table IV have, therefore, been re-examined, and average tearing strengths calculated utilizing only 5 peaks taken respectively from 5 successive intervals in the record, each interval representing ¼ in. of tearing. These values are given in Table V.

A comparison between Tables IV and V indicates that essentially the same average values are obtained whether these are calculated from 5 or 10 successive equal ¼-in. intervals of tearing. The reliability of the average values calculated from the smaller number of such intervals is somewhat less, but there would appear to be no other disadvantage in accommodating types of testing machines on which only a limited length of tearing can be recorded. The use of 5 peaks only from successive equal intervals of tear whose lengths should total not less than 1 in. might be found a satisfactory and practical compromise.

Appendix I

Description of Fabrics Used in This Study

No.	Fabric	Wt./yd.²	Construction	Canadian DND specification
15-3	Cotton twill (preshrunk)	6.8 oz.	70 × 56	(TEXT. 1-5-3)
19-3	Nylon canvas	5.75	107 × 40	(TEXT. 7-1-2)
20-2	Cotton utility	5.25	54 × 48	(TEXT. 1-3-1)
23-2	Rayon twill	3.75	120 × 70	(TEXT. 4-1-3)
24-2	Rayon acetate twill	2.4	86 × 86	(TEXT. 4-5-1)
25-4	Wool-filled serge	10.75	65 × 42	(TEXT. 3-2-1)
27-2	Nylon taffeta	2.6	157 × 90	(TEXT. 7-1-1)
28-2	Cotton poplin	4.5	109 × 41	(TEXT. 1-6-3)
96	Cotton sheeting (unbleached) (aeroplane fabric)	3.75	84 × 80	—
97	Cotton sheeting (unbleached) (drogue fabric)	3.0	52 × 53	—
98	Nylon (rip stop*)	1.0	122 × 114	—

* 15th, 16th and 17th, 18th ends (picks) woven two as one.

Appendix II

Canadian Government Specifications Board

Tearing Strength (Single Rip Method)
(Method 12.1 of Schedule 4-GP-2)
Revised 26 December, 1957

1. *Purpose and Scope*

1.1 This method is intended for use with woven fabrics as a means of determining resistance to tearing in the manner prescribed by the method. It is frequently referred to on the North American continent as the "tongue" method, a term which, in Great Britain, signifies procedures involving a double rip (see British Standards Institution Handbook No. 11, 1956, pages 165 and 167).

2. *Principle*

2.1 The force required to propagate a simple tear across one or more pieces of fabric is measured, the force being applied perpendicularly to the yarns ruptured in the tear.

3. *Apparatus*

3.1 A recording tensile testing machine of the inertialess type, or pendulum type as described in Method 9, having a suitable capacity and operating with the driven clamp moving at a speed of 12 ± 0.5 inches per minute (Note 1). Both gripping surfaces of the clamps shall measure 1 × 2 inches or more, with the longer dimension perpendicular to the direction of application of the load. The distance between the clamps at the start of the test shall be not more than 3 inches. The ratchet pawl of the pendulum-type machine shall be rendered inoperative during the test.

4. *Test Specimen*

4.1 Test specimens shall be cut 2 inches wide and not less than 8 inches long. Two sets of specimens are required, one set for warp tearing strength, having the longer dimension parallel to the weft yarns, and the other set for weft tearing strength, having the longer dimension parallel to the warp yarns. The number of specimens required shall be not less than five in each direction (Note 2). Specimens shall be cut in such a manner that no two weft-tearing specimens shall record the tearing of the same weft yarns, nor any two warp-tearing specimens the tearing of the same warp yarns. A cut 3 inches in length is made lengthwise in each specimen starting at the centre of one of the short edges, forming two 'tails' for clamping in the jaws of the testing machine. Depending upon the relationship between the tearing strength of the fabric and the capacity of the testing machine, multiple test specimens may be used (Note 3).

5. *Procedure*

5.1 The test specimens shall be conditioned in accordance with Method 2. One 'tail' of the specimen shall be clamped in the upper jaws of the testing machine and the other 'tail' clamped in the lower jaws in such a manner that the (originally adjacent) cut edges of the tails shall lie in the straight line joining the centres of the clamps, and the two tails shall present opposite faces of the fabric to the operator. The testing machine is then started and an autographic record obtained of the force required to tear a minimum of 3 inches of the test specimen.

5.2 Where it is found that the tearing force observed with a single specimen in a pendulum-type machine is less than 10 percent of the total capacity of the machine, two or more specimens shall be superimposed and clamped together in the machine and torn simultaneously (Note 3).

5.3 The autographic record obtained will indicate a succession of peak values of tension corresponding to the successive rupturing of yarns or groups of yarns in the course of the tear. A peak value, for the purpose of this method, is any point on the graphic record that exceeds in value the points both immediately preceding and following in the record. The highest peak value recorded in each of ten successive one-quarter inch intervals of tearing shall be noted, and these values averaged to determine the mean tearing force of the specimen or multiple specimen tested (Notes 4 and 5).

6. *Report*

6.1 The average force required for the continued tearing of single specimens shall be reported as the tearing strength (single rip method) of the sample (Note 6). If the average value calculated in para. 5.3 refers to a multiple specimen, this value shall be divided by the number of test pieces comprising the multiple specimen, in reporting the tearing strength. The machine type upon which the testing was carried out shall also be reported.

6.2 Irregular tearing behaviour, such as reversion of the tear to the cross-wise direction of the specimen or the withdrawal of cross-wise yarns from either 'tail' (yarn pull-out) during the test, shall also be reported (Note 5).

NOTE (1) Due to the presence of inertia factors in the pendulum-type of testing machine the values of tearing strength of a given fabric determined by this method on pendulum types and inertialess types of machine will usually differ. Such differences vary with the fabric under test and cannot be correlated by the application of any single numerical factor valid for fabrics in general.

NOTE (2) If the precision with which tearing strength is to be measured is specified, reference should be made to Method 1 of the Schedule for procedures to determine the number of test specimens required. If this is not known, the number of specimens indicated in para. 4.1 shall be taken.

NOTE (3) In cases in which the tearing strength of a single specimen is less than 10 percent of the capacity of the testing machine, multiple specimens consisting of two or more single specimens shall be used so as to provide a net tearing strength of at least 10 percent of the capacity of the testing machine. In such cases, however, not fewer than three such multiple specimens in each direction shall be tested.

NOTE (4) Frequently it will be found that an initial peak force substantially greater than subsequent maxima is required to initiate tearing. This initial maximum shall not be included in the calculation of the average tearing strength.

NOTE (5) In a 'regular' tear the cross-wise yarns are extended and ruptured successively along the line of tearing. It may frequently be found that occasional yarns pull out of either 'tail' instead of breaking in proper sequence. When this occurs, the tension recorded includes forces other than those required for regular tearing. This behaviour is readily detected by inspection of the specimens during or after tearing, and is probably a pecularity both of the fabric itself and of the test procedure. Either the portion of the record affected by this behaviour shall be rejected, or 'irregular' tearing behaviour of the fabric shall be reported.

NOTE (6) The average result for the specimens tested is an estimate of the true average for the material under test. A measure of the reliability of this estimate can be obtained by determining the confidence interval (Method 1, para. 4.2) within which the true mean will lie for any given probability.

Appendix III

Linen Industry Research Association

Wing (Single-Rip) Tear Test*

Introduction Note—This test is designed for those fabrics which fail to tear in the direction of the applied force when tested by the Tongue-Rip method.

Outline—The tearing strength of fabrics is measured on a tensile-strength cloth-tester by recording the maximum load observed whilst tearing through 1 inch of cloth. The winged shape of the specimen ensures that tear strengths across either warp or weft can be determined for all fabrics which are tearable in either direction in practice.

Apparatus—A constant-rate-of-traverse cloth tensile testing machine of a suitable range, and power-operated at a rate not exceeding 4½ inches per minute, with either dial or autographic recording.

* A brief note on this method appeared as a letter to the Editor of the *Journal of the Textile Institute* **47**, p. T609 (1956). This note, however, does not set forth the method in detail, and proposes an angle of 55° instead of 65° as "an optimum value chosen to serve the widest range of fabrics. . . ."

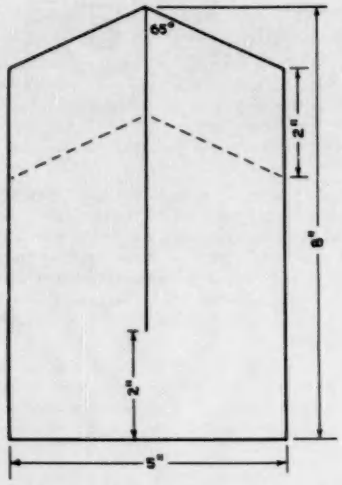

Fig. 1. Test specimen—wing rip.

Means for providing the atmosphere for testing specified in B.S. 1051, in which to condition and test the specimen. The atmosphere for testing has a relative humidity of 65 ± 2 percent, at 20 ± 2° C. (68 ± 4° F.).

Specimens—In the absence of detailed instructions in the material specification, ten specimens each 8 in. long and 5 in. wide shall be cut, with their sides parallel to the warp and weft threads, from positions distributed at random throughout the sample so as to represent adequately the material under test. Specimens should not include any part of the fabric within 2 in. of a selvedge and shall be taken so that the tear will be across the warp threads in five specimens and across the weft threads in five specimens.

A slit 6 in. long shall be cut down the centre of each specimen; the cut shall be parallel to the longitudinal threads and shall terminate at a transverse thread so as to leave a 2-inch portion of the fabric to be torn, as shown in Fig. 1. To assist in the alignment of the specimens in the machine clamps, the corners of the two wings are cut at an angle of 65 degrees to the central cut, and clamping lines marked in the wings as shown in Fig. 1.

Procedure—The testing machine shall be set with the jaws 7 in. apart, and if the machine is fitted with a rack and pawl to arrest the downward swing of the pendulum, the mechanism shall be made inoperative by securing the pawl clear of the rack.

The specimens shall be conditioned and the tests carried out in the atmosphere for testing.

The specimens are mounted in the machine by swinging the two wings outwards until their sloping ends are parallel; they are then clamped in the jaws of the machine, with the clamping lines marked on the wings placed centrally along the inner edges of the clamps.

The machine shall be operated and the specimen torn over a distance of 1 in. The highest reading on the dial shall be recorded as the tearing strength of that specimen.

Expression of Results—The mean of the five recorded values for tearing across the warp threads and the mean of the five recorded values for tearing across the weft threads shall be designated the tearing strength of the fabric across the warp and weft respectively.

If, during any test, the direction of tear transfers from that originally planned, the fabric shall be deemed to be untearable across the threads under test. The maximum load required to tear the specimen apart shall be recorded, but the direction of the tear shall be made clear.

9th December, 1955.

Acknowledgment

The author wishes to acknowledge the benefit of helpful discussions with members of CGSB Subcommittee H on the Revision of Test Methods for Textiles and also the assistance of Mr. R. A. Scythes in the experimental studies here described.

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Comparison of Methods for Determining Intrinsic Viscosities from Non-Newtonian Viscosities

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Abstract

Absolute flow curves for solutions of two samples of cotton cellulose at concentrations of 0.1, 0.2, and 0.3 g./100 ml. in 0.5 *M* cupriethylenediamine were determined over a shear stress range of 0.01–1000 dynes/sq. cm. Both rotational and capillary viscometers were employed. All three solutions behaved as Newtonian fluids below a shear stress of 1.0 dyne/sq. cm.

Various methods of calculating intrinsic viscosities were investigated. Values based on zero shear rate viscosities are required to avoid dependence on the viscometric procedure. Where determination of intrinsic viscosities is not the primary objective, the best method for precise differentiation among closely similar samples appears to be comparison of apparent viscosities using a single high concentration and as low a standard shear stress as practicable. Intrinsic viscosity determinations, based on non-Newtonian viscosities, are less satisfactory.

INTRINSIC viscosity, through its relationship with the average degree of polymerization (D.P.) of the solute, is an important property of polymer solutions. Its precise determination is complicated by the fact that even very dilute solutions may be non-Newtonian. Over the shear rate range normally encountered in a series of viscosity determinations in the laboratory, changes in the apparent viscosity[3] due to non-Newtonian behavior may easily obscure changes due to a D.P. change.

These considerations are important in assessing degradation of cellulose incurred in mill processes for converting natural cotton to yarn. The existence of this source of degradation has been reported in earlier papers [8, 9, 15, 16] but the viscometric determinations of intrinsic viscosity changes were based upon an empirical correction for the non-Newtonian effects.

The work reported here was undertaken to compare various methods used to detect small differences among the intrinsic viscosities of relatively similar samples of cotton cellulose and, thereby, to confirm or deny conclusions drawn from previous studies. To serve as a basis for the comparison, absolute flow curves of two of the samples previously studied were determined over a wide shear rate range.

A rotational viscometer was specially constructed to determine the flow curves in the low shear rate region where the Newtonian properties appear to prevail [11] and thus measure directly zero shear rate viscosities. High shear rate portions of the curves were obtained with capillary viscometers. Using the absolute flow curve data, various computational methods which have been suggested to compensate for the effect of variation of apparent viscosity with shear rate were compared. Zero shear rate viscosities served as the standard.

Viscometers

Rotational Viscometer

The rotational viscometer, Figures 1 through 5, bearing marked similarity to the Couette type, was designed for measurements at very low shear stresses. It was operated over a shear rate range of approximately 0.02–100 sec.$^{-1}$ and a shear stress range of approximately 0.01–100 dynes/sq. cm. The princi-

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[3] The term *apparent viscosity*, as used in this paper, refers to a "viscosity" calculated from the viscometric data by use of an equation developed for computing viscosities of Newtonian liquids, i.e., Poiseuille's equation for a capillary viscometer and Margule's equation for a rotational viscometer.

ples of operation of a Couette viscometer are well described in several texts on viscometry [2, 7, 10].

During operation the bob is supported entirely by the torsion wire. This form of suspension, which requires no bearings, was chosen to obtain maximum possible sensitivity at very low shear stresses. A disadvantage is instability of the bob at high shear rates. The resulting wobble begins at a shear rate of approximately 50 sec.$^{-1}$; the actual critical value depends upon viscosity.

All parts of the bob and cup assembly are stainless steel. Pertinent dimensions are length of bob, 7.958 cm.; diameter of bob and of guard rings or plugs, 4.464 cm.; diameter of cup, 5.114 cm.; vertical clearance between bob and guard rings at outer surface of bob, 0.60 mm.

During operation the cup rotates while the guard rings remain stationary. The angular displacement of the bob caused by the torsional drag of the solution is measured by rotating the torsion wire head until the bob returns to its zero stress position. A telescope-mirror-scale system, with the mirror mounted on the bob stem, is used to check the position of the bob. The cup is driven by a synchronous motor through a gear box converted from a multispeed "Mono-drum" chart drive. Twenty-two different speeds are obtainable from 0.0242 to 468.0 r.p.m., with a ratio between successive speeds of 1.600.

The instrument was designed to measure absolute viscosities. Absolute accuracy was checked using water and two N.B.S. standard viscosity oils of viscosities of 6 and 17 cp. Viscosities computed from Margule's equation were 2.1% greater than the true values. Since the standard deviation of a single measurement under normal operating conditions was found to be 0.7%, this positive deviation (or bias) was too large to attribute to random errors. It was also too large to attribute to errors in dimensions or in calibration of the torsion wires. It was independent of both rotational speed and viscosity and was therefore attributed to fluid drag on the ends

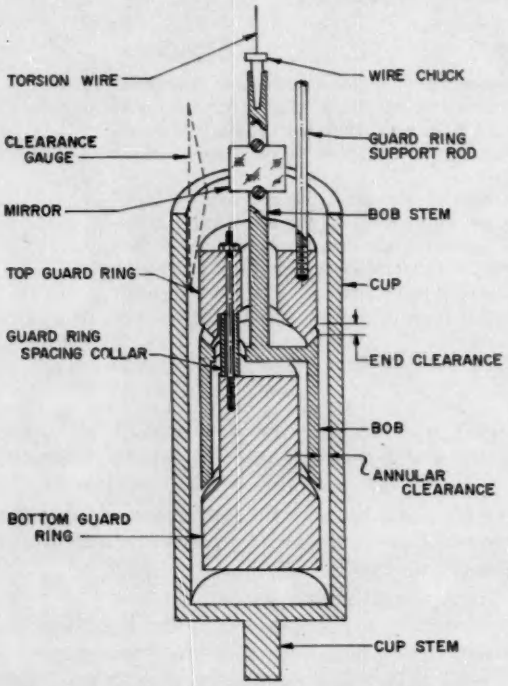

Fig. 1. Sketch of bob and cup assembly (not to scale).

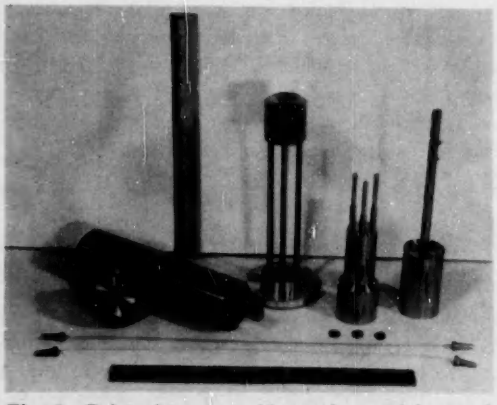

Fig. 2. Bob and cup assembly, torsion pendulum, and torsion wires.

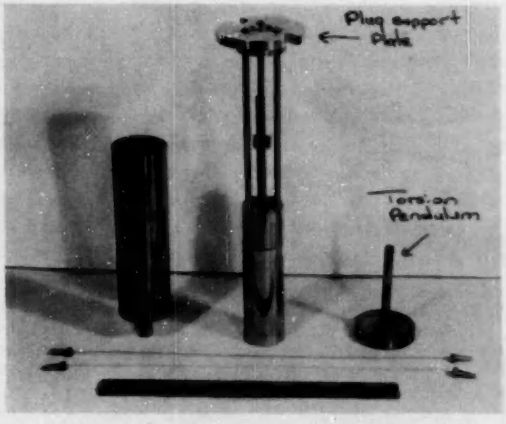

Fig. 3. Cup, bob, and guard ring assembly, torsion pendulum, and torsion wires.

of the bob, not entirely eliminated by the guard rings. Since the error was independent of shear rate, a correction factor of 0.98 was applied to calculated shear stresses based on actual bob dimensions.

The torsion wires which supported the bob were calibrated with a torsion pendulum of weight equal to the weight of the bob minus the weight of the fluid it displaced. The wires used were 0.005-in. diameter steel piano wire, and 0.010- and 0.020-in. diameter perma-nickel spring wire. Relaxation of the wires during operation of the viscometer was found to be negligible if measurements in individual runs were taken in order of increasing speed, thus measuring the smallest deflections first.

Capillary Viscometers

Two stock Cannon-Fenske viscometers were used, a #50 and a #100. Capillary radii were calculated from the weights of mercury contained in measured lengths. Volumes of the bulbs were similarly determined. The natural or potential heads, H_o, were found by a method essentially the same as that of Bury [10], which corrects for kinetic energy effects. The empirical coefficient m for use in the correction term in the modified form of Poiseuille's equation, Equation 2, was determined by calibration with water and the two N.B.S. standard viscosity oils. The lengths of the capillary tubes, L, were determined last by solving Equation 2 for L using data obtained from runs with water, values of all other variables having been previously determined. The values of L were calculated rather than measured, since it was not possible to account otherwise for the effect of the flared ends.

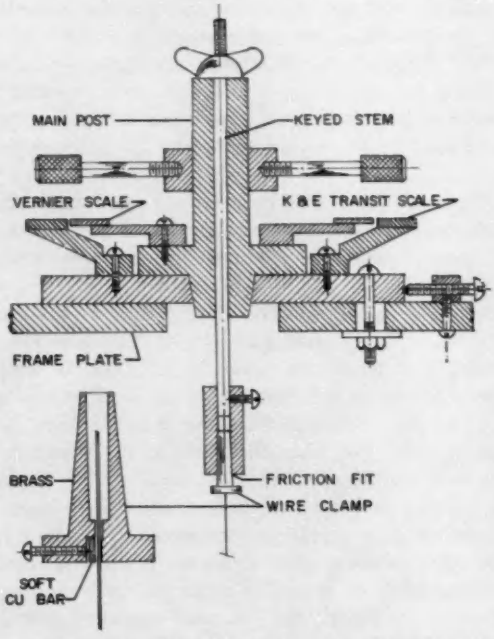

Fig. 4. Sketch of torsion head (not to scale).

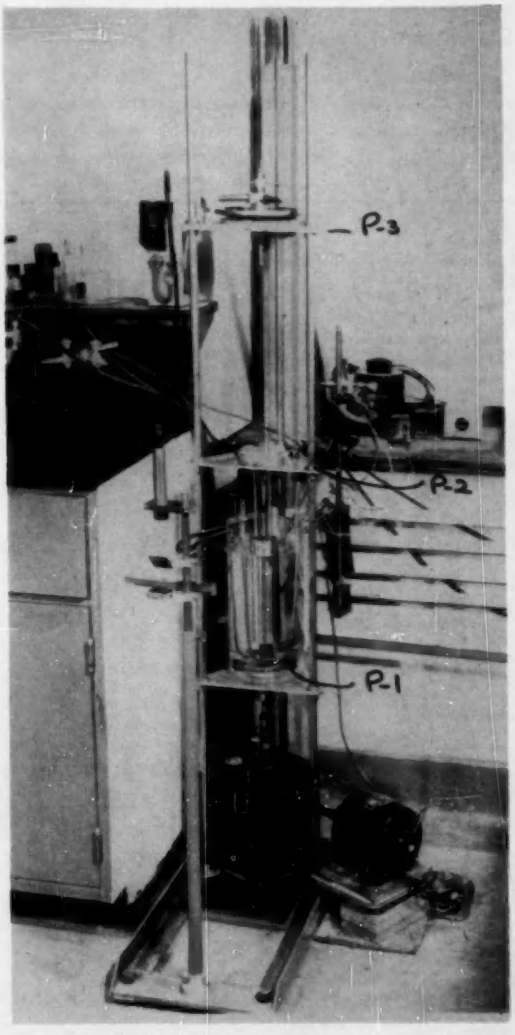

Fig. 5. Rotational viscometer.

Experimental Procedure

Cotton Samples

The two cottons were from the same general source, a single bale previously described [15]. One sample was directly from the bale and the other, designated 1-H, had been deliberately overprocessed by eight passes through a carding beater. While sampling methods for these cottons are as previously described [15], exact duplication of the intrinsic viscosities cannot be expected, due to the long period of storage between the original tests and the ones reported here.

Preparation of Solutions

Solutions of 0.1, 0.2, and 0.3 g. of cotton in 100 ml. of 0.5 *M* cupriethylenediamine were prepared in 200-ml. quantities. Concentrations were based on dry weights. The procedure and equipment were the same as described by Whitwell and Schwenker [16], except that agitation was improved by use of baffled flasks, and possible evaporation loss during the solution period was reduced by passing the purified nitrogen stream through a tower containing 0.5 *M* cupriethylenediamine immediately before it entered the dissolving flask.

Attempts to prepare 0.4 g./100 ml. concentrations were unsuccessful. Even with dissolving times of 10 hr., complete solution of such samples could not be obtained consistently. It was concluded that only partially degraded samples of the original cottons could be completely dissolved at this concentration. This limit on concentration is of special interest in view of the recommended concentration of 0.5 g./100 ml. in a standard test [1].

Viscometry

The two Cannon-Fenske viscometers were each charged with 10-ml. aliquots; 155 ml. was required in the rotational viscometer. Transfer of solution to, and operation of, the capillary viscometers were identical to that described by Whitwell and Schwenker [15]. Their apparatus, modified to permit application of higher pressures, was employed in this work.

In order to exclude oxygen during filling of the rotational viscometer, purified nitrogen was admitted to the bottom of the cup through a stainless steel tube. A soft rubber cap in the top of the cup, fitted around the support rods and bob stem, provided a means of collecting the displaced gas which was then conducted to an oxygen-indicating Zimmerman fog trap.

Since it was necessary for the rubber cap to be removed during operation of the viscometer, air was in contact with the solution during experimental measurements. In order to determine whether or not oxidative degradation during a run was significant, a 0.2 g./100 ml. solution was run for a period of 2 hr., several times longer than the duration of a normal run. At the end of the 2-hr. period samples were removed from the space between the bob and cup, i.e., from that level in the viscometer where degradation would affect results. No degradation was detected; the viscosities of the samples, measured in a capillary viscometer, were identical with those of the original solution. It was concluded that diffusion of degraded molecules or of oxygen from the surface to the bob level was negligible in the time required for experimental measurements.

Nomenclature

For capillary viscometers:

H	total head ($H_0 + H_a$)
H_0	natural head
H_a	applied head
L	length of capillary
P	total pressure ($P = H\rho g$)
R	capillary radius
V	volume flowing through capillary in time t
m	coefficient of kinetic energy term
r	intermediate radius, $r < R$
t	flow time

For rotational viscometer:

L	length of bob
b	radius of bob
c	radius of cup
r	intermediate radius, $b < r < c$
Ω	rotational speed of cup

General:

C	solution concentration
Z	slope of flow curve on logarithmic coordinates
g	acceleration of gravity
k	numerical constant
ζ	viscosity counterpart
η	Newtonian viscosity
η_0	solvent viscosity
η_r	relative viscosity
η_{sp}	specific viscosity
$[\eta]$	intrinsic viscosity
η_z	zero shear rate viscosity
ρ	density of solution
τ	shear stress
du/dy	shear rate

Dissolving flasks and viscometers were submerged in constant temperature baths at 25.00° ± 0.03° C. during all operations.

Experimental Data

Duplicate solutions of each concentration of each of the cottons were prepared separately and run in both the rotational and capillary viscometers. A third sample was also run in the case of the 0.2 g./100 ml. bale sample. To cover the necessary shear stress range with adequate precision, some of the samples were run in both capillary viscometers, while torsion wires of different characteristics were used during rotational viscometer runs.

Complete tables of the original data are reported elsewhere [3]; although too extensive for tabulation here, all experiments are summarized in Figure 6.

Absolute Flow Curves

For Newtonian fluids, the equations required for translating experimental measurements into viscosities are those of Margule for rotational viscometers, Equation 1, and of Poiseuille for capillary viscometers, Equation 2. The latter includes a correction term for kinetic energy and end effects. Both equations are based on Newton's definition of the absolute flow curve of a Newtonian fluid, Equation 3, where η is the desired viscosity coefficient.

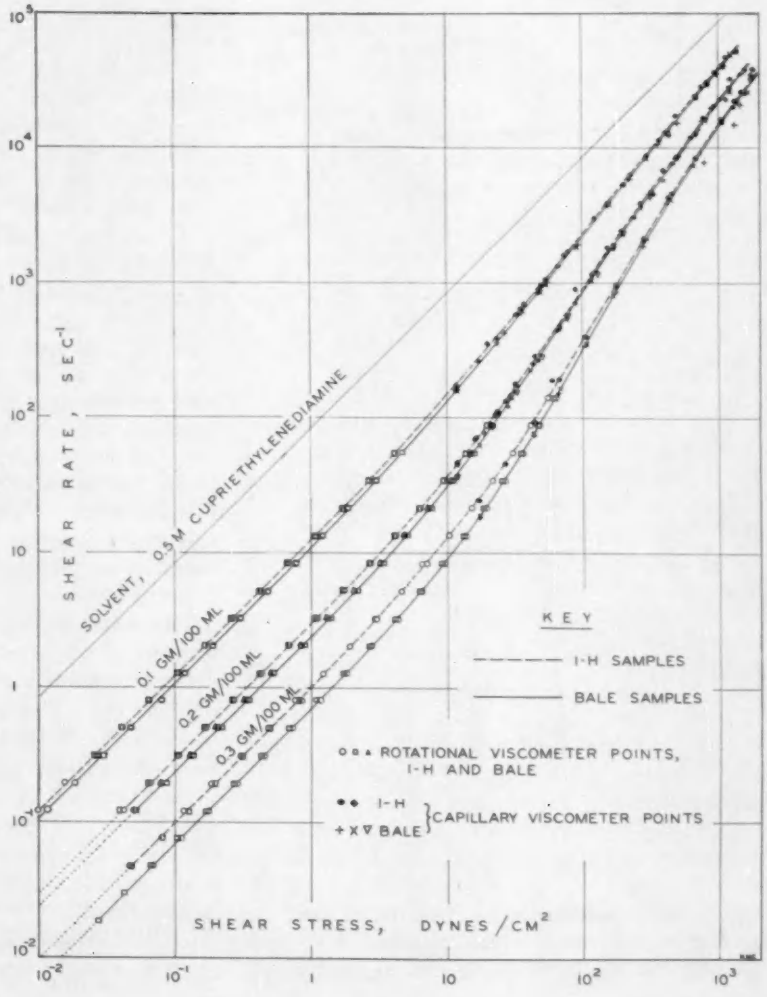

Fig. 6. Absolute flow curves. Solutions of cotton in cuprietheylenediamine.

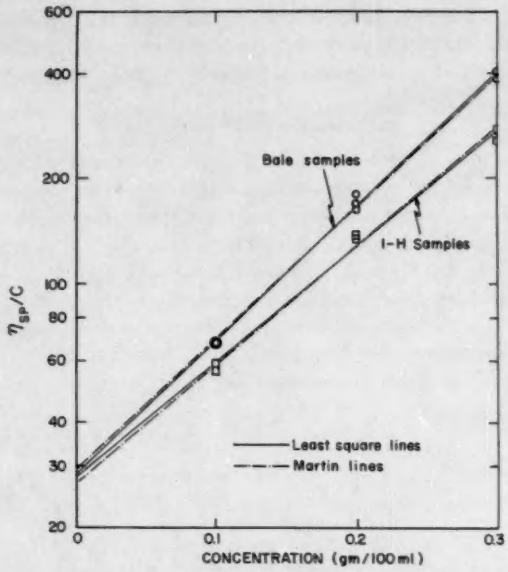

Fig. 7. Reduced viscosity vs. concentration. Zero shear rate viscosity method.

$$\eta = \frac{T(c^2 - b^2)}{4\pi L\Omega c^2 b^2} \tag{1}$$

$$\eta = \frac{\pi R^4 H g \rho t}{8\,V\,L} - \frac{m\rho V}{8\pi L t} \tag{2}$$

$$\frac{du}{dy} = \frac{1}{\eta}\,\tau \tag{3}$$

Shear rates and shear stresses are usually calculated at the wall of a viscometer; however, they can be calculated with equal validity at any intermediate radius. The following equations for shear rate and shear stress apply at any radius r where $r \leqslant R$ in the case of the capillary viscometer and where $b \leqslant r \leqslant c$ in the case of the rotational viscometer; b and c are bob and cup radii respectively.

Rotational: $$\left(\frac{du}{dy}\right)_r = \frac{2\,b^2 c^2 \Omega}{r^2(c^2 - b^2)} \tag{4}$$

$$\tau_r = \frac{T}{2\,\pi\,L\,r^2} \tag{5}$$

Capillary: $$\left(\frac{du}{dy}\right)_r = \frac{4\,V}{\pi\,R^3\,t}\left(\frac{r}{R}\right) \tag{6}$$

$$\tau_r = \frac{H\,g\,\rho\,r}{2\,L} \tag{7}$$

A previous publication [4] has shown how the last four equations can be used to calculate absolute flow curves of non-Newtonian liquids if proper values of the intermediate radius r are used. Choice of the proper intermediate radius has been explained. The flow curves calculated from the experimental data in this manner are plotted in Figure 6. They are similar to those reported by other workers for other polymer solutions [11, 13]. The intermediate radii used were 2.380 cm. for the rotational viscometer and $0.79R$ for the capillary viscometers. A correction factor of 0.98, previously explained, was introduced into the numerator of Equation 5. A value of H, equal to the experimental value less that portion used in overcoming K.E. and end effects, was used in Equation 7.

It can be readily shown that this method of calculating absolute flow curves is equivalent to the use of the Weissenberg equation for the capillary viscometer and to the correction factor of Philippoff and Gaskins [12] for the rotational viscometer. The main difference lies in the choice of position at which to compute values of shear rate and shear stress. The investigators just cited choose the wall; the previous article by the present authors selects a suitable radius within the fluid.

The curves from the rotational viscometer data are believed to be accurate within the limits of precision previously stated (standard deviation of 0.7% with error due to approximate method of calculation negligible by comparison). Accuracy of the curves from the capillary viscometer data at high shear rates and shear stresses (e.g., greater than 10,000 sec.$^{-1}$ or 60 dynes/sq. cm.) is uncertain. These limits correspond to points where the correction term of Equation 2 amounts to 2% of the main term. The fact that the curves obtained from the two viscometers coincided where they overlapped is taken as a confirmation of the absolute accuracy in that region of the plot.

Two points regarding the curves are of particular interest. First, for all three concentrations they are Newtonian below a shear stress of about 1.0 dyne/sq. cm. Below this critical shear stress, the curves have a slope of 1.0 and are linear (on double logarithmic coordinates). Apparent viscosities of these solutions determined in any type of viscometer would therefore be the true zero shear rate viscosities if the maximum local shear stress in any part of the instrument did not exceed 1.0 dyne/sq. cm. Subsequently, in this paper, zero shear rate viscosities determined from the low shear stress linear portions of the flow curves will be denoted by η_z.

The second point of interest is that the percentage difference between point viscosities [4] of the bale and 1-H samples increases with both increasing concentration and decreasing shear stress. The difference is a maximum in the low shear stress region of the 0.3 g./100 ml. solution.

Calculation of Intrinsic Viscosities and Discussion of Results

Various portions of the viscometric data obtained for determining the absolute flow curves have been employed to compare a variety of methods suggested for evaluating intrinsic viscosities of polymers which form non-Newtonian solutions. In all cases the intrinsic viscosities were determined by extrapolating the logarithm of the reduced viscosity, plotted against concentration, to zero concentration. Calculational procedures, being similar, are outlined in detail only for the first method.

In the first four cases least squares lines were used for extrapolation and the results analyzed statistically. In the same four cases the parameters of the Martin equation, of the form

$$\log (\eta_{sp}/C) = \log [\eta] + k [\eta] C \qquad (8)$$

were also estimated, using the method of least squares.

From Zero Shear Rate Viscosities (η_z)

Values of η_z, for each sample of each cotton at each concentration, were obtained from the rotational viscometer data for the low shear stress Newtonian portions of the flow curves. Relative viscosities, η_r, and specific viscosities, η_{sp}, were calculated as follows:

$$\eta_r = \eta_z/\eta_0 \qquad (9)$$

where η_0, the viscosity of the solvent, was 1.20 cp.

$$\eta_{sp} = \eta_r - 1 \qquad (10)$$

Reduced viscosities, η_{sp}/C, were then calculated. Least squares lines for $\log(\eta_{sp}/C)$ vs. C were used for extrapolating the data to zero concentration to obtain the intrinsic viscosities. Three hypotheses were considered:

1. There is no difference between the bale and 1-H points; therefore, a single line will represent all points.

2. Separate lines exist for bale and 1-H samples, and they are unrelated.

3. The Martin equation satisfactorily fits the bale and 1-H data; i.e., reduced viscosity lines, so calculated, are not distinguishable from those drawn for Hypothesis 2.

The results of the least squares calculations are summarized below. The reduced viscosity lines for the second and third hypotheses are shown in Figure 7.

	Source	Sums of squares	Degrees of freedom	Mean squares
(a)	Deviations from a single least squares line	0.05067	11	
(b)	Deviations from individual least squares lines (minimum residual)	0.003362	9	0.000373
(c)	Deviations from Martin lines	0.003947	10	0.000395
	Deviations resulting from sample differences, (a) − (b)	0.04731	2	0.02365
	Test I: $_2F_9 = 0.02365/0.000373 = 63.4^{***}$			
	Deviations resulting from use of Martin lines instead of individual least squares lines, (c) − (b)	0.000585	1	0.000585
	Test II: $_1F_9 = 0.000585/0.000373 = 1.56$			

Test I indicates that the probability of Hypothesis 1 being as valid as Hypothesis 2 is less than 0.1%. Test II, although statistically weak, does not justify rejection of Hypothesis 3; hence the Martin equation is accepted as an adequate means of representing both samples.

The values of the intrinsic viscosities obtained from the individual least squares lines and from the Martin lines, and the value of the constant k in Martin's equation, are recorded in Table I. Results of the statistical tests for the zero shear rate method and three other methods are summarized in Table II.

In the determination of intrinsic viscosities it is desirable to eliminate the effects of both shear rate and concentration in order to obtain a value characteristic of the solute molecules at rest in an infinitely dilute solution. The method just described is the only one of the various methods tried that satisfactorily eliminated the shear rate variable. Since the reduced viscosity plots were essentially linear, it

[4] The term point viscosity, defined here, is the ratio of shear stress to shear rate for a specific point on the flow curve. It is to be distinguished from apparent viscosity, previously defined.

TABLE I. Intrinsic Viscosities

Method	From least-squares lines			From Martin lines			
	Bale	1-H	Decrease	Bale	1-H	Decrease	Value of k
Zero shear rate viscosities	28.5	27.8	0.7	29.6	26.7	2.9	0.127
Viscosity counterpart	27.8	27.3	0.5	29.1	26.1	3.0	0.189
Average shear rate (ASTM)	28.8	29.1	−0.3	29.8	28.2	1.6	0.0412
Apparent viscosities at H_0	20.5	19.8	0.7	20.8	19.4	1.4	0.172
Hall and Fuoss (graphical, not least-squares)	21.5	19.0	1.5				

TABLE II. Statistical Tests

Method	Test I			Test II		
	F ratio	Degrees of freedom	Probability that samples are identical	F ratio	Degrees of freedom	Probability that Martin Eqn. fits data*
η_s	63.4	2, 9	0.0001	1.56	1, 9	0.27
Counterpart	29.4	2, 11	0.0001	0.5	1, 11	†
ASTM	3.16	2, 11	0.088	0.5	1, 11	†
H_0	69.8	2, 11	0.0001	0.75	1, 11	†

* Probability that Martin equation does not impose additional significant variance over that represented by least-squares lines.

† An F ratio of 1.0 indicates no added variance due to the imposition of the Martin equation as a restriction. An F ratio of less than 1.0 is in this case interpreted as being identical to a ratio of 1.0.

might be concluded that their extrapolation to zero concentration eliminated the concentration variable. The latter conclusion has not been checked here; no work was done with concentrations under 0.1 g./100 ml.

Viscosity-Counterpart Method [8, 9]

Frequently, for non-Newtonian high polymer solutions, the relation

$$\frac{du}{dy} = \frac{1}{\zeta}(\tau)^z \qquad (11)$$

will be a good approximation of the flow curve over an appreciable shear stress range. Evaluation of ζ, for a specific range not including unit shear stress, is then equivalent to extrapolating the experimental data to unit shear stress in order to obtain ζ as the reciprocal of the intercept. The extrapolation is performed using logarithmic coordinates for shear rate and shear stress. The value of ζ thus obtained is an empirical constant rather than a fundamental property of the solution.

It has been demonstrated [8, 9] that use of ζ in place of apparent viscosities in the determination of intrinsic viscosities yields linear reduced viscosity plots suitable for extrapolation to zero concentration. The method was proposed for use with capillary viscometer data obtained under a practical working range for applied heads of 0–50 cm. of water. The original capillary viscometer data within this range were used in computing the results reported in Tables I and II. A kinetic energy and end effect correction was employed.

Calculated intrinsic viscosities agree well with those from the zero shear rate method, and the two samples were distinguished, although not as sharply as with the zero shear rate and ΔH_0 methods. When used to distinguish between samples, the method appears to be excessively complicated and suffers from extrapolation over almost twice the range covered by the data (11–60 dynes/sq. cm.). The extrapolation is serious, since variance of the intercept depends upon the square of the distance from the mean value. Moreover, the curve is not truly linear, and the extrapolated mean value thus depends upon spacing of shear stresses at which data are taken. Since linearity must be assumed, measurements should be concentrated at the ends of the usable shear stress range rather than distributed over it. Unfortunately, extension of the range toward unit stress for im-

proving precision is not practical, due to operating limitations with the capillary viscometers.

Average Shear Rate Method

In the ASTM method [1] for determining degradation of cotton and intrinsic viscosities, the latter are calculated by an empirical equation from the apparent viscosities of 0.5 g./100 ml. solutions determined from capillary viscometer data at an apparent average shear rate of 500 sec.$^{-1}$. The average shear rate is defined as

$$\left(\frac{du}{dy}\right)_{ave} = \frac{8\ V}{3\ \pi\ R^3\ t} \qquad (12)$$

The apparent fluidity, the reciprocal of the apparent viscosity, at the standard average shear rate is obtained by linear interpolation or extrapolation on a logarithmic plot of apparent fluidity vs. average shear rate.

The same data used in the viscosity counterpart method were employed, and intrinsic viscosities were determined from the apparent viscosities at the standard average shear rate. Corrections for kinetic energy and end effects were applied. Results are reported in Tables I and II.

Difficulties inherent here are similar to those with the counterpart method: frequent extrapolation and nonlinear relationships. An additional problem is the specification of a high shear rate and consequent high shear stress, which tends to reduce the ability of the method to differentiate between samples. It should be noted that the shear stress is calculated at the wall, while the average shear rate occurs, obviously, within the fluid mass.

From Apparent Viscosities at ΔH_0

Apparent viscosities were calculated from the data for each capillary viscometer run at zero applied head for the #100 Cannon-Fenske viscometer. Since both a #50 and #100 viscometer were used in the actual work, flow times observed in the former had to be converted to equivalent flow times for the latter using the absolute flow curve data for the conversion. Accuracy of the conversion is believed to be excellent since the flow times were long enough to make kinetic energy effects negligible. The shear stress at the wall in the #100 viscometer at natural head is 21.8 dynes/sq. cm., so this method is equivalent to computing intrinsic viscosities from apparent viscosities at standard wall shear stress of 21.8 dynes/sq. cm. Results are reported in Tables I and II.

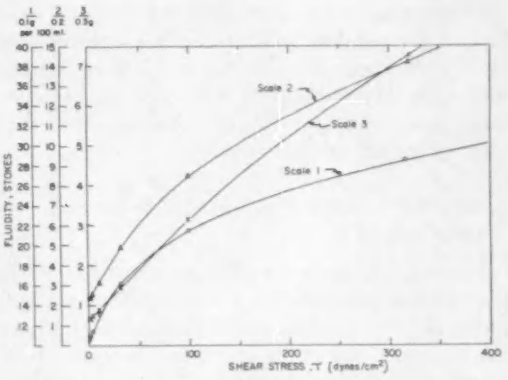

Fig. 8. Point fluidity vs. shear stress, bale samples.

The shear stress was well above the critical transition from Newtonian flow, causing low values of the resulting intrinsic viscosities. Distinction between samples is of the same order as obtained by the zero shear rate method and is better than that of any of the other methods investigated. The high precision is undoubtedly due to the simplicity of the method. No interpolation or extrapolation is required in the calculations and the experimental procedure does not require regulation of applied heads. For the single purpose of distinguishing between samples, it is the best method.

Method of Hall and Fuoss [6]

These investigators found that a plot of $1/Pt$ vs. P was linear over a much wider range of flow rates than in the Pt vs. $1/t$ plot frequently used to eliminate kinetic energy effects. The proposed form also was shown to correct for drainage effects. Values of Pt at zero P were therefore recommended for determining relative viscosities. Intrinsic viscosities determined therefrom were shown to be independent of the conditions of viscosity measurement.

The deviations from Newtonian character of the cellulose solutions reported here are considerably greater than those of the solutions of polystyrene used by Hall and Fuoss. The difference is important since the lines on the suggested coordinates are not straight. The values reported in Table I were obtained by approximating straight lines through the experimental points, but the method was obviously inapplicable to the cotton data.

Since $1/Pt$ is proportional to $1/Ht$, and the latter

is proportional to a point fluidity, the Hall and Fuoss method is equivalent to assuming that a plot of point fluidity vs. shear stress is linear. Figure 8 shows such a plot for the current data over a shear stress range of 0 to 300 dynes/sq. cm. The nonlinear character of the relationship is evident.

From Point Viscosities at Constant Shear Rates and Shear Stresses

Figures 9–11 show the effect of arbitrary selection of either standard shear rate or standard shear stress on the absolute value of intrinsic viscosity. The specific viscosities for developing these figures are based on point viscosities calculated as the ratio of shear stress to shear rate at the designated shear stress or shear rate. Curves based on apparent viscosities would be very similar to those plotted.

It is obvious from Figure 9 that any extrapolation of η_{sp}/C vs. C at constant shear rate leads to intersecting lines, an incomprehensible physical situation.

The hump in the shear rate curve of Figure 11 further emphasizes the difficulties inherent with this parameter. The hump is due to the existence of a critical stress, previously discussed, identical for all solutions. When point viscosities for the three concentrations for the constant stress plot are measured at a series of steadily increasing shear stresses, they all start to decrease at the same stress with the result that the intrinsic viscosity determined from these point viscosities also decreases. When they are measured at a series of increasing shear rates for the constant rate plot, the point viscosity for the most concentrated solution starts to decrease first, then that for the intermediate concentration, and finally that for the lowest concentration. The result of the latter behavior is that the reduced viscosities for the more concentrated solutions decrease more rapidly with increasing shear rate than those for the less concentrated solutions. On the reduced viscosity plot, this pivots the line around the lowest or lower concentration points, thus raising the value of the intercept at zero concentration. The intercept is the intrinsic viscosity. The magnitude of this rise is

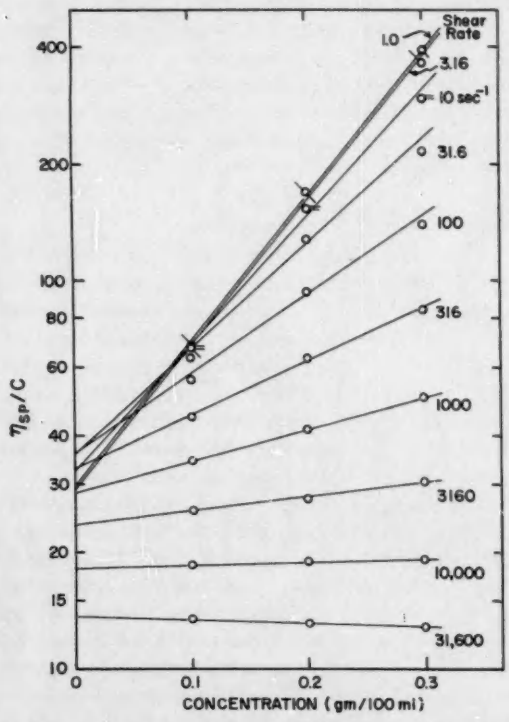

Fig. 9. Reduced viscosity vs. concentration. Point viscosities at fixed shear rates, bale samples.

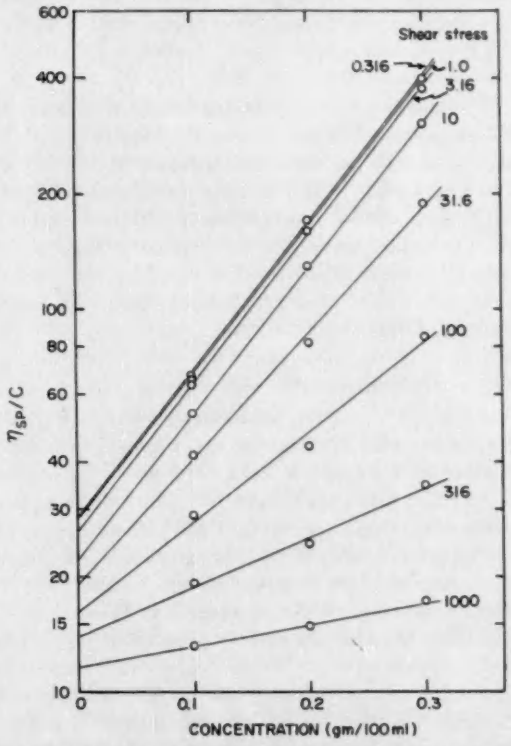

Fig. 10. Reduced viscosity vs. concentration. Point vicosities at fixed shear stresses, bale samples.

obviously dependent upon the concentration coordinates on the reduced viscosity plot. As a result of this behavior, intrinsic viscosities determined at constant shear rates are dependent not only upon the particular shear rate but also upon the particular concentrations of the solutions, at least in that shear rate range which includes and is immediately adjacent to the hump. An analogous concentration dependence does not apply to the constant stress curve; hence a constant stress method is preferable to a constant rate method.

Other Extrapolation Methods

In some cases [5, 14] it has been found that a plot of log η_{sp} against shear rate is linear. Figure 12 shows such a plot for the low shear rate portion of the flow curve of the 0.1 g./100 ml. bale sample. Log η_{sp} is curved when plotted against either shear rate or shear stress. Neither type of plot is satisfactory for extrapolation of the current data to zero shear rate.

Plots of viscosity and specific viscosity against shear rate and shear stress on linear coordinates proved to be similarly unsatisfactory.

The Martin Equation

Martin lines were fitted to the data in the four cases analyzed statistically. Within the limits of Test II of Table II, the Martin lines appear to fit the data; however, a more sensitive test can be made by comparing the ratios of the mean squares for deviations of means from the regression lines to deviations due to replicates. Such a test showed about a 5% probability that the Martin equation is a good model. This result is not too surprising or disappointing, since the equation is to a large extent empirical. The discrepancy, while significant, does not appear too serious, particularly since extrapolation to zero concentration is known to yield intrinsic viscosities which are only relative with respect to D.P. An advantage of using the Martin equation despite its demonstrated limitations is the unification of the data for several samples into a single calculation. The slopes and intercepts applicable to each sample are obtained from all the data from all samples; greater precision results than when each sample is treated as a separate entity.

Martin, working principally with cellulose of lower molecular weight than cotton cellulose, found that the value of the constant k in his equation was 0.130 when the equation was written in terms of logarithms to base 10. The value obtained in this work by use of zero shear rate viscosities was 0.127.

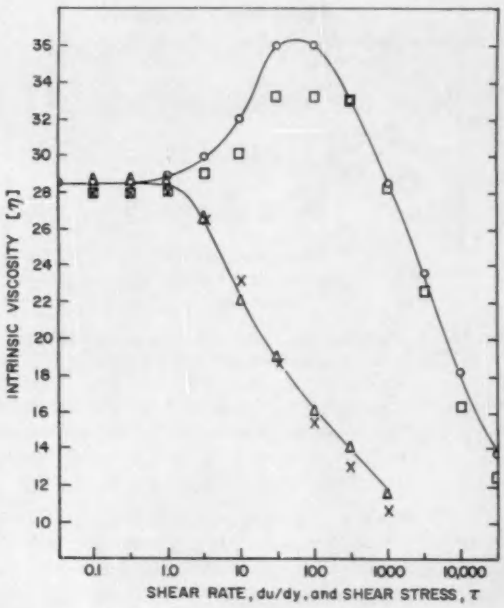

Fig. 11. Effect of choice of standard shear rate or shear stress on intrinsic viscosities.

Conclusions

A principal objective of this work was a comparison of various methods used to calculate intrinsic viscosities from viscosity measurements made in capillary viscometers. The zero shear rate method, based on rotational viscometer data, appears to be the only method that provides intrinsic viscosity estimates that are independent of the method of viscosity measurement. It is a necessary condition that the maximum local shear stress in the instrument should not exceed 1.0 dyne/sq. cm. in the case of the solutions employed in this study. The type of capillary viscometer used operates in the range of 10 dynes/sq. cm. and higher. Although the viscosity-counterpart and average shear rate methods yielded intrinsic viscosities essentially the same as those obtained by the zero shear rate method, an adverse recommendation seems essential in either case, since the precision of either method is exceedingly sensitive to the details of the experimental procedure.

When the objective is differentiation between samples and measurement of the difference, determina-

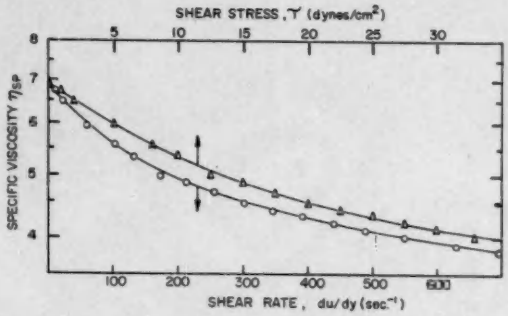

Fig. 12. Log η_{sp} vs. shear rate and shear stress, bale samples, 0.1 g./100 ml.

tion of intrinsic viscosities by any of the methods tested appears to be an unnecessarily complex procedure. For the samples used in this work, there was a small difference in intrinsic viscosities but a large difference in solution viscosities and reduced viscosities. The difference was greater the higher the concentration and the lower the shear rate at which viscosities were measured. The easiest and probably the most precise comparison is in terms of the apparent or reduced viscosities measured in a single capillary viscometer at a single shear stress and at a single concentration, as previously noted [15]. This type of comparison would be valid only for samples which are essentially similar; i.e., where the flow curves of the various samples belong to the same family of flow curves. It would certainly be valid for determining degradation of one type of cotton but not necessarily for comparing different types of cotton.

Maximum sensitivity would be obtained by comparing samples at a relatively high concentration and a low shear stress. Choice of shear stress, rather than shear rate as the standard, is preferable, since the former can be automatically and precisely reproduced in each run in kinematic viscometers constructed to yield the desired stress at their natural head. Use of a standard shear rate requires two or more runs and determination of the required flow time by interpolation of the data.

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Topochemical Mechanisms Involved in the Preparation and Deacetylation of Partially Acetylated Cottons

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Abstract

Iodine sorption and moisture sorption data and some density, x-ray, and infrared data have been obtained on partially acetylated (PA) cottons before and after progressive deacetylation with 2 *N* hydrochloric acid or with *N*/2 sodium hydroxide. The results substantiate the accepted theory that in the partial acetylation of cotton the amorphous regions are acetylated first. They also show that deacetylation of PA cottons by these two reagents proceeds by different mechanisms. With hydrochloric acid, the acetylated amorphous cellulose is deacetylated more or less completely throughout the fiber before the acetylated crystalline is attacked. With sodium hydroxide both are deacetylated simultaneously with little or no selectivity, so that deacetylation proceeds annularly from the surface of the fiber inward.

The properties of the original PA cottons differed markedly from those of the same acetyl content obtained by deacetylation. The properties depended further upon the reagent used for deacetylation and on the acetyl content before deacetylation. These differences in properties can be attributed to differences in the proportions and distribution of amorphous, crystalline, acetylated amorphous, and acetylated crystalline cellulose within the fiber and also to differences in the fine structure, degree of lateral order, and stress patterns resulting from the inhomogeneity of the volume changes which take place during acetylation or deacetylation.

THE topochemical reactions involved in the partial acetylation of native cellulose fibers have been discussed frequently in the literature; the consensus is that the amorphous regions are acetylated before the crystalline regions [5, 24]. The triacetylation of the amorphous regions spreads the cellulose chains so that the acetylation can proceed into the crystalline regions.

Considerable work has been published on the mechanisms involved in the saponification of fibrous acetylated cellulose by alkalies, and opposing theories have been advanced. The results in the various reports are not always comparable since the work is based, in some instances, on partially acetylated natural fibers; e.g., PA cottons, and, in other instances, on synthetic acetate fibers, such as acetate rayon. In the experiments on PA cellulose, proponents of the opposing views are Happey [6, 7] and Zilahi and Oswald [24]. Happey saponified PA cotton and PA ramie and, on the basis of x-ray data, reached the conclusion that the more readily accessible portions are deacetylated before the acetylated crystalline regions are attacked. More recently, Zilahi and Oswald investigated the saponification of PA cotton with boiling Na_2CO_3 solution. On the basis of moisture regain and electrical resistance data and the dyeing behavior of fiber cross sections, they reached the conclusion that the saponification takes place independently of the microheterogeneous structure of PA cotton and proceeds annularly from the outside of the fiber inward.

Acid hydrolysis of PA native celluloses apparently has never been investigated from this point of view.

The purpose of the present investigation was to obtain further information on the topochemical mechanisms involved in the preparation and subsequent deacetylation of PA cottons. Iodine sorption and moisture sorption data have been obtained for various degrees of acetylation and deacetylation. The deacetylation was accomplished by hydrolysis with 2 *N* hydrochloric acid or by saponification with

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N/2 sodium hydroxide at room temperature. A limited amount of density, x-ray, and infrared data has also been obtained. The results from the two methods of deacetylation indicate that different mechanisms are involved. With hydrochloric acid, the acetylated amorphous regions are deacetylated first; with sodium hydroxide, the deacetylation proceeds by the annular mechanism.

Experimental Methods

The iodine sorption procedure used for these experiments was a modification of that described by Schwertassek [18, 20]. Since the method is of an empirical nature, the duplication of results depends primarily on a strict adherence to the chosen experimental conditions.

The details of the procedure were as follows. Warp and filling threads were stripped from the fabric samples and were cut into $\frac{3}{8}$-in. lengths with sharp-edged scissors. Portions slightly greater than 0.3 g. were placed in open weighing bottles over P_2O_5 in a desiccator attached to a mechanical pump for evacuation overnight. The accurate weights of the dried samples were obtained. The closed bottles were stored in the desiccator over P_2O_5.

Since the extent of sorption is dependent on the temperature [2], the iodine sorption experiments were performed in a constant temperature room, controlled to 23° ± 0.5° C. Onto the dried cotton samples, 1.2 ml. of I-KI solution (5 g. I_2 + 40 g. KI + 50 ml. H_2O) was dropped from a combination microvolume and weight burette. The material was worked well with a small glass pestle so as to insure uniform distribution of the iodine solution throughout the sample. The bottle was closed and allowed to stand for 2 hr.

The iodine-soaked sample was transferred to a wide-mouthed glass-stoppered flask into which 80 ml. of a nearly saturated solution of Glauber's salt had been measured from a 100-ml. burette. Since a saturated solution of Glauber's salt presented manipulative difficulties by occasional crystallization of the salt in the burette or pipette, a slightly less concentrated solution was used. The concentration was kept constant by adjusting to a specific gravity of 1.160 as tested with a 60° F./60° F. hydrometer. The pestle and weighing bottle were rinsed quantitatively into the flask with the remaining 20 ml. of Glauber's salt solution from the burette. All the samples thus prepared were shaken for 1 hr. on an automatic shaker together with duplicate blanks each of which contained 100 ml. of Glauber's salt solution plus a weighed 1.2 ml. of I-KI solution. From each flask, a 75-ml. aliquot was pipetted into a flask and titrated with 0.02 *N* sodium thiosulfate, using starch solution as the indicator. The pipettes were fitted with filter tips packed with glass wool to exclude fiber particles from the titration liquid.

The titration of the blanks established the exact concentration of the iodine solution in milligrams of iodine per gram of I-KI solution. The difference between the calculated weights of iodine added to the sample and of iodine washed off into the Glauber's salt solution was converted to milligrams of iodine sorbed per gram of sample (corresponding to the AZ value of Schwertassek). This in turn was converted to the "iodine sorption value" (ISV), milligrams of iodine per gram of anhydroglucose residue, by means of the formula $\text{ISV} = \frac{\text{AZ}}{100 - \text{B}}$, where B is the percent acetyl on a dry sample-weight basis. Preliminary experiments proved that the acetyl percentage of the sample was the same before and after the iodine sorption measurement.

The Eberstadt method as modified by Genung and Mallatt [4] was used to determine percent acetyl in the acetylated and partially deacetylated samples. After equilibrating by adsorption under standard conditions (70° ± 2° F. and 65% ± 2% RH), the percent moisture regain was calculated for the various samples from the loss in weight after drying in a forced draft oven for 5 hr. at 105° C. Both sets of data were usually converted from the dry weight basis (dw) to the anhydroglucose-residue basis (ahg) by the formula $\%_{ahg} = \%_{dw}/(100 - \text{B})$. Thereby, the acetyl content or the moisture sorbed is shown as grams of acetyl or water per 100 g. of anhydroglucose residue.

The x-ray and infrared data were obtained by the methods of Segal, Martin, and Creely [23] and O'Connor, DuPré, and Mitcham [11], respectively. Density determinations were made by the gradient column method of Orr, Weiss, Moore, and Grant [12].

Samples

Seven 80–100-yd. portions of a commercial sheeting, after being desized and scoured, were partially acetylated by the jig method [1, 3] to obtain seven different PA fabrics ranging in acetyl content from

TABLE I

Fabric number	Acetyl as percentage of: Dry weight, dw	Anhydroglucose residue, ahg*	Degree of substitution, DS†
0	0.0	0.0	0.00
1	4.6^{5}	4.8^{8}	0.18^{4}
2	7.4^{8}	8.0^{8}	0.30^{4}
3	8.2^{8}	9.0^{3}	0.33^{9}
4	14.0^{6}	16.3^{6}	0.61^{4}
5	16.7^{4}	20.1^{1}	0.75^{4}
6	22.4^{2}	28.9^{0}	1.08^{1}
7	27.2^{4}	37.4^{4}	1.39^{8}

* $\%_{ahg} = \%_{dw}/(100 - \%_{dw})$.
† $43.044/(162.14 + 43.044\ DS) = \%_{dw}/100$.

4.7% to 27.2%, dry weight basis. Briefly, the process involves an activation by presoaking in glacial acetic acid followed by acetylation with an acetic anhydride–acetic acid mixture using perchloric acid as the catalyst. These seven fabrics with the unacetylated, desized, and scoured control formed the fundamental basis for this study. Their acetyl contents, which have been expressed in different ways in the course of the discussion of the results, are given with the sample designations in Table I. These samples were from the same fabric bolts as those used in previous investigations [8, 9].

The deacetylated samples were prepared by steeping the PA fabrics at ambient room temperature (27° ± 4° C.) in 2 *N* hydrochloric acid for 1–48 days, or in *N*/2 sodium hydroxide for ¼ to 4 hr. All deacetylated samples were washed thoroughly and air dried before testing.

Results and Discussion

Iodine Sorption

Acetylation. All the acetylated samples sorbed more iodine than the unacetylated control, and the sorption increased in direct proportion to the acetyl content. Under the empirical conditions as outlined for the procedure, a high correlation (+0.99986) exists between the iodine sorption value, ISV (milligrams of iodine per gram of anhydroglucose residue), and the acetyl content (grams of acetyl per 100 grams of anhydroglucose residue). The iodine sorption values are the averages of 5–8 determinations

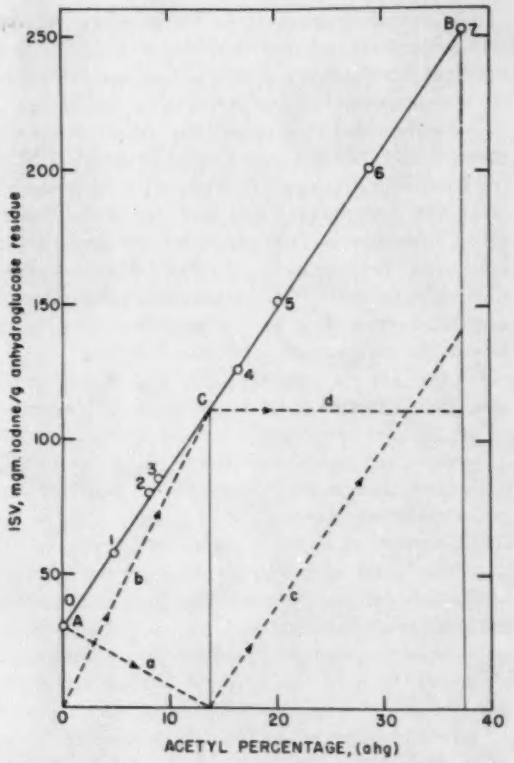

Fig. 1. Iodine sorption value vs. percent acetyl for PA cotton Samples 0–7. Dashed lines represent schematically the individual contribution of each constituent to the total ISV, assuming all amorphous cellulose is triacetylated at C: *a*, amorphous cellulose; *b*, acetylated amorphous cellulose; and *c*, acetylated crystalline cellulose.

with a standard deviation ranging from 1 to 4 ISV units. The regression line, calculated from the averages, is defined by the equation

$$ISV = 5.938\ (\%\ acetyl_{ahg}) + 30.5$$

and is represented in Figure 1 by the line AB which was terminated at the values for Sample 7. Throughout the discussion of ISV, AB will be referred to as the "acetylation line."

It is generally agreed that when PA cottons are prepared by a process such as the present one, which involves preswelling in glacial acetic acid, the amorphous cellulose is acetylated to the triacetate before the crystalline cellulose is attacked appreciably. In the interpretation of the results, therefore, it would be advantageous to have an approximate value for the percentage of the cotton which might be termed amorphous or accessible.

The values reported in the literature for the percent amorphous cellulose in cotton as determined by different methods vary over a wide range. A reason for the variations is given in the recent publication of Marchessault and Howsmon [10], which shows that there is a gradation in the fine structure of cellulose from extreme disorder (amorphous) to extreme lateral order (crystalline) and that part of the "amorphous" fraction as determined by one method may behave as "crystalline" by another. However, from their data, these authors conclude that a sharp transition from crystalline to noncrystalline may be an acceptable approximation for native fibers.

In the present investigation, the choice of an amorphous-fraction value based upon the properties of the samples investigated seemed appropriate. In a previous investigation of this series of fabrics [9], a marked change in properties and behavior was noted in the neighborhood of 15% acetyl (ahg). An acetyl content of 13.6% (ahg) was accepted as the transition point after consideration of the acid deacetylation data, to be presented later. Therefore, the assumption has been made that all the amorphous cellulose is triacetylated at 13.6% acetyl, which implies that 17% of the original cotton behaves as amorphous and 83% as crystalline cellulose.

Since the cellulose within the crystalline lattice does not sorb iodine, the iodine sorbed by the unacetylated cotton (ISV = 30) can be attributed wholly to the amorphous or accessible cellulose present [19, 21]. At 13.6% acetyl (C, Figure 1), all the amorphous cellulose has been replaced by triacetylated amorphous cellulose, so that the iodine sorption (ISV = 111) at this degree of acetylation was due entirely to the triacetylated amorphous cellulose. Thus, it is apparent that, under the conditions of the iodine sorption measurements, the sorption capacity of triacetylated amorphous cellulose was 3.7 times as great as that of unacetylated amorphous cellulose.

An inherent weakness of measuring ISV by this technique lies in the uncontrolled concentration of the iodine solutions at equilibrium. The final iodine concentration under the experimental conditions for a 13.6% acetyl sample, for example, was less than that for the unacetylated sample. If the two iodine sorption values were measured at the same iodine equilibrium concentration, the observed sorption capacity of the triacetylated amorphous cellulose would be somewhat greater than 3.7 times that of the unacetylated amorphous cellulose.

Some limited data had been obtained to show the manner in which the iodine sorption of the various samples varied with the equilibrium concentration. Analysis of these data justified the construction of a schematic diagram to represent, as a first approximation, the contributions made to the total iodine value by the individual components. In Figure 1, for example, the iodine sorptions of the samples between 0 and 13.6% acetyl, represented by AC, have been considered as the sum of that for the triacetylated amorphous cellulose (line *b*) and that for the residual amorphous cellulose (line *a*). Similarly, for acetyl percentages above 13.6%, the values on CB represent the sum of the contributions made by the acetylated amorphous (line *d*) and by the acetylated crystalline cellulose, assuming triacetylation (line *c*).

Assuming triacetylation, the relative iodine sorption capacities of amorphous cellulose, acetylated amorphous cellulose, and acetylated crystalline cellulose, estimated from the slopes of lines *a*, *b*, and *c*, are in the approximate ratio of 1:3.7:2.7. On this basis, the sorbing capacity of acetylated amorphous would be about 1.3 times that of acetylated crystalline cellulose. This value is, of course, somewhat high because the measurements were not made at the same equilibrium concentration.

Deacetylation. Figure 2 shows the changes in ISV as Samples 7, 6, 5, and 4 were deacetylated to various acetyl contents by steeping at room temperature in 2 *N* hydrochloric acid or in *N*/2 sodium hydroxide. In both parts of the figure, AB is the acetylation line of Figure 1. The marked difference in the effect of these two reagents shows that different mechanisms must be involved in the two methods of deacetylation.

HYDROCHLORIC ACID.—The hydrochloric acid deacetylation curves all tend to coincide with the acetylation line until approximately the same quantity of acetyl (14%, ahg) has been removed. Sample 4 (16.4% acetyl) may be considered as containing practically no acetylated crystalline cellulose. Since the deacetylation curve for this sample, in which only the amorphous cellulose has been acetylated, retraces the acetylation line until almost all of the acetyl has been removed, the iodine sorption capacity of deacetylated amorphous cellulose, i.e., the "restored" amorphous, must be approximately the same as that of the original unacetylated amorphous cellulose. The fact that the deacetylation curves for Samples 5, 6, and 7 also approximate the acetylation line

until about the same quantity of acetyl has been removed leads to the conclusion that, in all these samples, the acetylated amorphous cellulose was deacetylated before the acetylated crystalline cellulose was attacked appreciably.

After the removal of acetyl from the amorphous region, further deacetylation by hydrochloric acid to any given acetyl content resulted in an ISV higher than that for the sample of the same acetyl content on the acetylation line. Consequently, when the acetylated crystalline cellulose was deacetylated, the product had a marked iodine sorption capacity and probably consisted primarily of a noncrystalline cellulose. As deacetylation progressed further, the deviation from the acetylation line increased to a maximum and eventually decreased sharply as deacetylation neared completion. As might be expected, the deviation at the maximum was greatest for Sample 7, which, in this group, would yield the greatest amount of deacetylated crystalline cellulose; this deviation is progressively less for samples of lower acetyl content until the increase in sorption for Sample 4 is significant only by analogy, since the deviation of the experimental ISV from the acetylation line is scarcely larger than the experimental error.

The final marked decrease in iodine sorption can be explained by an increase in crystallinity and consequently a reduction in sorption sites, caused by the hydrolytic attack of hydrochloric acid on amorphous cellulose [14]. This increase in crystallinity has been considered the sum of two effects, so-called [21] "false increase," resulting from the removal of short-chain fragments from the amorphous regions, and a "true increase," resulting from the alignment of the broken chains into crystalline array.

After the samples were steeped in 2 *N* hydrochloric acid, the ISV (30) of the original unacetylated cotton dropped to 28 in 1 day, to 23 in 10 days, to 20 in 21 days, and to 19 in 48 days. The effect of hydrochloric acid can be expected to be somewhat greater for the amorphous cellulose formed by deacetylation, since this is in a more swollen state, never having been dried. This may explain the fact, not mentioned above, that during the removal of the first 13–14% acetyl the deacetylation curves in Figure 2 show a slight tendency to fall below the acetylation line. It also accounts for the decided drop in ISV at lower acetyl contents, where the proportion of amorphous cellulose is greater and the exposure to the acid was for much longer periods. For example, after 10 days in acid the ISV of Sample 7 was 103

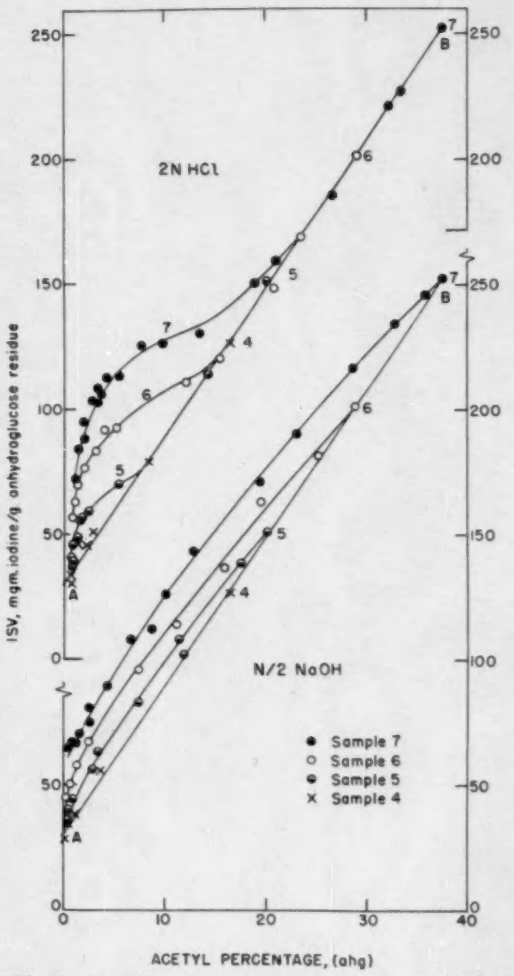

Fig. 2. Iodine sorption value vs. percent acetyl for PA cottons partially deacetylated by 2 *N* HCl or *N*/2 NaOH. AB is acetylation line of Figure 1.

at an acetyl content of 3%, but after 48 days its ISV was only about 70 at 1% acetyl.

The above interpretation of the hydrochloric acid deacetylation mechanism has been represented schematically to show the iodine sorption as the summation of the contributions by the various components in the sample; e.g., Figure 3 illustrates the acid deacetylation of Sample 7 (37% acetyl). As shown in Figure 1, the amorphous, the acetylated amorphous, and the acetylated crystalline portions contributed 0, 111, and 142 units, respectively, to the ISV (253) of the original sample. After the removal of acetyl from the amorphous region (point D at

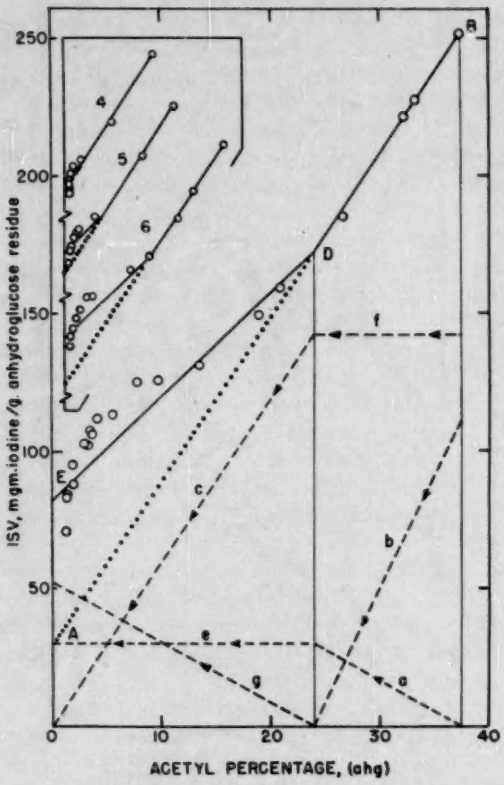

Fig. 3. Comparison of HCl-deacetylation data for Sample 7 with schematically derived ISV curve, assuming all the acetylated amorphous cellulose has been deacetylated selectively at D. AB is acetylation line of Figure 1. Dashed lines represent the contribution of each constituent to the total ISV: *a* and *e*, restored amorphous; *b*, acetylated amorphous; *c* and *f*, acetylated crystalline; and *g*, additional amorphous formed from acetylated crystalline cellulose. Insets show corresponding comparisons for Samples 6, 5, and 4.

23.7% acetyl), the resultant sample had an ISV of 172, the sum of 30 (the restored amorphous) and 142 (the acetylated crystalline, which as yet had not been appreciably attacked). Therefore, as the deacetylation progresses from 37% to 24%, the ISV (line BD) can be considered to be the sum of the contributions by the restored amorphous (line *a*), the residual acetylated amorphous (line *b*), and the acetylated crystalline (line *f*).

On further deacetylation, the acetylated crystalline is deacetylated and the contribution of the residual acetylated crystalline follows line *c*, while that of the restored amorphous is constant (line *e*). If the assumption is made that acetylated crystalline is deacetylated to a completely amorphous product which has the same iodine sorption capacity as the restored amorphous, the contribution of this additional amorphous would follow line *g*. Therefore, the ISV for the sample after deacetylation to values below 23.7% acetyl would follow line DE, the sum of lines *c*, *e*, and *g*.

The experimental data, represented by open circles in Figure 3, show good agreement with the theoretical lines BD and DE for the greater part of the deacetylation. An explanation has already been offered for the slight drop below BD.

For acetyl values just below 12%, the observed sorptions were above those predicted by DE. This could be interpreted as indicating that the amorphous formed from the acetylated crystalline cellulose has a higher iodine sorption capacity than the original amorphous. Another explanation could be based on the formation of an intermediate cellulose acetate in accordance with the theory of Rosset and Paris [15, 16, 17]. Their experimental data showed a maximum dye sorption at an overall acetyl content corresponding to the monoacetate after the partial deacetylation of an acetate rayon by ammonium hydroxide. There is also a possibility that the apparent deviation results from nonvalidity of one or more of the assumptions upon which the construction of the schematic diagram is based.

The final drop in ISV can be explained by the rapid increase in crystallinity after prolonged exposure to the acid and, pursuing the Rosset and Paris theory, by a decrease in the amount of cellulose at the stage of acetylation which produces maximum sorption.

The data for Samples 6, 5, and 4 (insets in Figure 3) show the same type of agreement with the schematic diagrams.

SODIUM HYDROXIDE.—Zilahi and Oswald [24] have shown that the deacetylation of partially acetylated cotton by boiling 0.1 *M* sodium carbonate is microhomogeneous and annular in nature; i.e., the deacetylation progresses from the periphery of the fiber inward in annular fashion, the acetyls being removed from the amorphous and crystalline portions more or less simultaneously with little or no selectivity. Rosset and Paris [15] also report an annular saponification of cellulose acetate fibers by *N*/2 sodium hydroxide. This nonselectivity with alkaline solutions as opposed to the apparent selectivity of the acid solution explains the difference between the hydro-

chloric acid and the sodium hydroxide deacetylation curves.

Unlike the hydrochloric acid curves, the sodium hydroxide deacetylation curves lie above the acetylation line from the very beginning of the deacetylation. This would be anticipated, assuming as before that the products formed by deacetylation of acetylated crystalline and acetylated amorphous have the same iodine sorption capacity. The acetylated amorphous was shown to have an iodine sorption capacity about 30% greater than that of the acetylated crystalline cellulose. Therefore, if a given amount of acetyl is removed from both acetylated celluloses simultaneously, a smaller decrease in ISV would be expected than if an equal amount of acetyl were removed from the acetylated amorphous cellulose alone.

Figure 4 shows schematically the iodine sorption values which would be predicted for the sodium hydroxide deacetylation of Sample 7 by this mechanism on the basis of the same assumptions used in constructing Figure 3. Thus, the ISV contributions of the acetylated crystalline, of the acetylated amorphous, and of the amorphous at 37.4% acetyl are 142, 111, and 0, respectively; after complete deacetylation, the contributions of the "restored" amorphous and of the "additional" amorphous (i.e., that formed from the acetylated crystalline) are 30 and 52, respectively. Since the two forms of acetylated cellulose are deacetylating simultaneously, lines *c* and *b* represent the contributions to the ISV of the residual acetylated crystalline and the residual acetylated amorphous cellulose, respectively, throughout the deacetylation. Concurrently, the restored amorphous cellulose and the deacetylated crystalline cellulose are adding their contributions; the former progresses along line *a*, which must terminate (0% acetyl) at an ISV of 30, and the latter along the line *g*, which terminates at an ISV of 52 if the deacetylation product of the acetylated crystalline has the same iodine sorbing capacity as the restored amorphous. BF represents the sum of the four components at each degree of acetylation. The experimental data are in satisfactory agreement with this theoretical line down to about 7% acetyl. At lower acetyl values, the experimental ISV decreases more rapidly than the theoretical line indicates.

The data for Samples 6, 5, and 4 (insets in Figure 4) show the same type of agreement with the schematic diagrams.

In contrast to the results after hydrochloric acid deacetylation, the experimental values after sodium hydroxide saponification never rise significantly above the values predicted from the schematic lines. This would indicate that the product formed by sodium hydroxide saponification of the acetylated crystalline cellulose has the same iodine sorption capacity as the restored amorphous.

Moisture Sorption

The difference in the mechanism of deacetylation by hydrochloric acid and by sodium hydroxide is reflected in the moisture sorption data, as shown by the results for these samples before and after deacetylation (Figure 5). The line ACB connects the values for the acetylated samples and will be referred to as the acetylation curve. A rather abrupt change

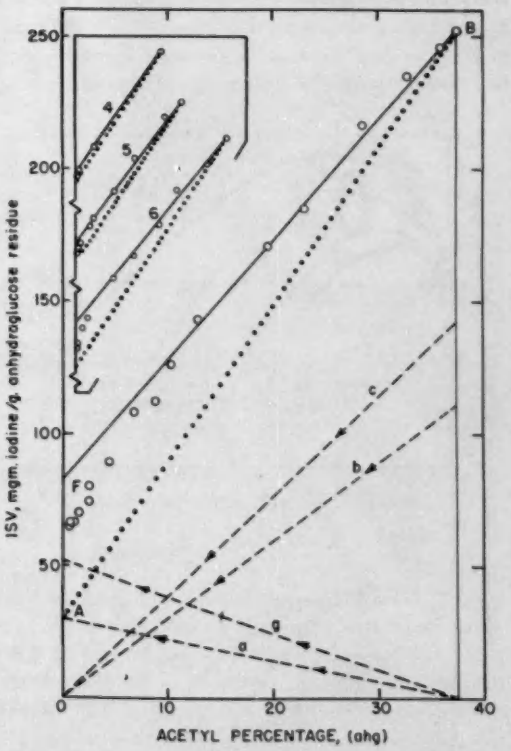

Fig. 4. Comparison of NaOH-deacetylation data for Sample 7 with schematically derived ISV curve, assuming deacetylation by annular mechanism. AB is the acetylation line of Figure 1. Dashed lines represent the contribution of each constituent to the total ISV: *a*, restored amorphous; *b*, acetylated amorphous; *c*, acetylated crystalline; and *g*, additional amorphous formed from acetylated crystalline cellulose. Inset shows corresponding comparisons for Samples 6, 5, and 4.

in slope comes in the vicinity of Sample 4, and this break was drawn, in conformance with the ISV graphs, at the point which corresponds to the complete triacetylation of the amorphous cellulose; i.e., at 13.6% acetyl, ahg. The solid lines show the changes in moisture sorption for each sample as the deacetylation proceeds. The moisture sorptions are calculated on the anhydroglucose-residue basis.

Hydrochloric acid deacetylation. The change in moisture sorption, on the basis of less complete data, has already been discussed [9]. Except for a few samples which had been exposed to the acid for very long periods, all the deacetylated samples had markedly higher moisture sorptions than the directly acetylated samples of the same acetyl percentages. Since the transformation of the amorphous to triacetylated amorphous cellulose resulted in a decrease in moisture sorption from 6.5 to 4.4%, a difference of 2.1%, a like increase in moisture sorption might be expected with the restoration of the amorphous; i.e., after removal of 13.6% acetyl. The observed increases were significantly greater than 2.1% and were greatest for the most highly acetylated samples, being 3.5% for Samples 7 and 6, 3.1% for Sample 5, and 2.6% for Sample 4. Consequently, the moisture sorption of the "restored" amorphous can be characterized as significantly higher than that of the original amorphous. The fact that no such difference was found in their iodine sorption capacities may be explained by assuming that, in the conditioned fibers, a higher degree of laterial order exists in the original amorphous than in the restored amorphous but that this difference is indistinguishable when the samples are subjected to swelling by immersion in the aqueous iodine solution.

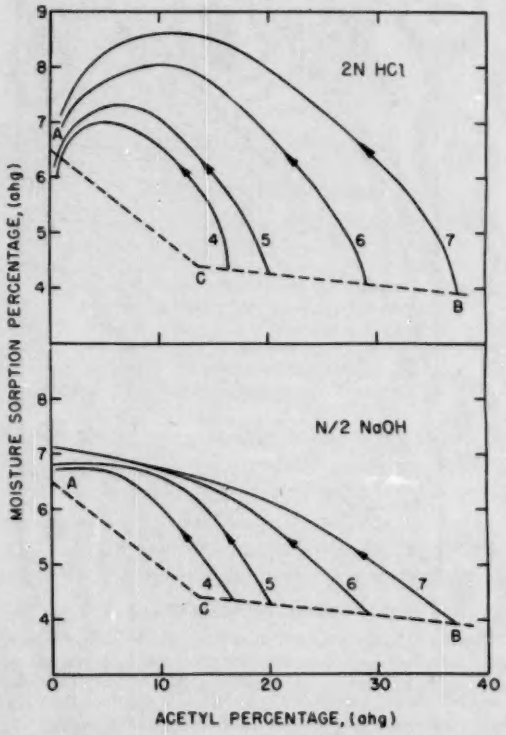

Fig. 5. Moisture sorptions of Samples 7, 6, 5, and 4 after deacetylation to various acetyl contents by 2 *N* HCl and by *N*/2 NaOH. Dashed lines connect values for original PA cottons.

The moisture sorption curve for each sample rises to a maximum which is highest (8.6%) for the sample of highest original acetyl percentage and appears after 3 or 4 days in the acid. The decrease in moisture sorption, after longer periods in the acid, can be explained by the increase in crystallinity caused by the hydrochloric acid. The original unacetylated sample, for example, showed a progressive loss in moisture sorption, decreasing from 6.5 to 5.5% after 48 days in the acid.

Sodium hydroxide deacetylation. The moisture sorption curves for samples deacetylated with sodium hydroxide follow a different pattern. Here the sorption rises more gradually with the loss of acetyl and reaches a final value slightly higher than that of the original unacetylated sample, regardless of the original acetyl content. There was no evidence of the decrease in moisture sorption at very low acetyl percentages which was noted after hydrochloric acid deacetylation. Neither was there a drop in moisture sorption in the unacetylated sample after exposure to the sodium hydroxide solution. Except for very low acetyl percentages, the moisture sorption resulting from alkaline saponification was less than that from hydrochloric acid hydrolysis at any given acetyl percentage. This indicates that a higher degree of lateral order exists in the cellulose formed by the alkaline saponification.

X-Ray and Infrared Measurements

The relative degrees of crystallinity of various acetylated and deacetylated samples were estimated from x-ray diffraction measurements by the method of Segal, Martin, and Creely [23] and from infrared measurements by the method of O'Connor et al. [11]. Neither of these methods for determining

crystallinity has been fully developed or standardized for use on chemically modified cottons, and no correction factor is known yet for the dilution effect of the added acetyl. Nevertheless, the results show some interesting qualitative relationships.

The results are summarized in Figure 6, in which the "crystallinity index," CI, is plotted against acetyl percentage (dry weight basis). $CI_{(x\text{-}ray)}$ has been defined [23] as $100\,(I_{002} - I_{am})/I_{002}$, where I_{002} is the intensity of the 002 interference of cellulose I and I_{am} is the average intensity at $2\theta = 18°$. $CI_{(infrared)}$ has been defined [11] as $A_{6.9\mu}/A_{11.0\mu}$, where $A_{6.9\mu}$ and $A_{11.0\mu}$ are the base-line corrected absorbances of the band maxima at about 6.9μ and 11.0μ, respectively. For unsubstituted celluloses, both of these indexes have been found to be closely correlated with the degree of crystallinity [11, 22, 23].

In these figures, percent acetyl on the dry weight basis rather than on the anhydroglucose basis was chosen as the abscissa, since the indexes are based on data for the whole samples without taking into account the possible dilution effect of the acetyl. In each graph, the data for the original samples indicate that the degree of crystallinity decreases as the acetyl content is increased. The rate of change is less marked during the first stages of acetylation, as would be expected if the amorphous cellulose were acetylated first.

The x-ray data for Sample 7 (27% acetyl, dw; 37% acetyl, ahg) at various stages of deacetylation confirm a number of conclusions drawn from the ISV and moisture sorption data, including the fact that deacetylation by hydrochloric acid and by sodium hydroxide proceeds by different mechanisms. With hydrochloric acid, there was very little change in the crystallinity index until the acetylated amorphous had been deacetylated. Deacetylation of the acetylated crystalline cellulose resulted in a definite increase in crystallinity, but at a rate which indicated that both amorphous and crystalline cellulose were being formed. Finally, at low acetyl contents, there was a marked increase in crystallinity which can be attributed to the hydrolytic attack of the acid on the amorphous cellulose. With sodium hydroxide, on the other hand, all the deacetylated samples showed a higher degree of crystallinity by the x-ray method than did the hydrochloric acid sample of the same acetyl percentage.

The same general conclusions can be drawn from the infrared data, with the exception that here no significant difference is shown between the behavior of hydrochloric acid and sodium hydroxide.

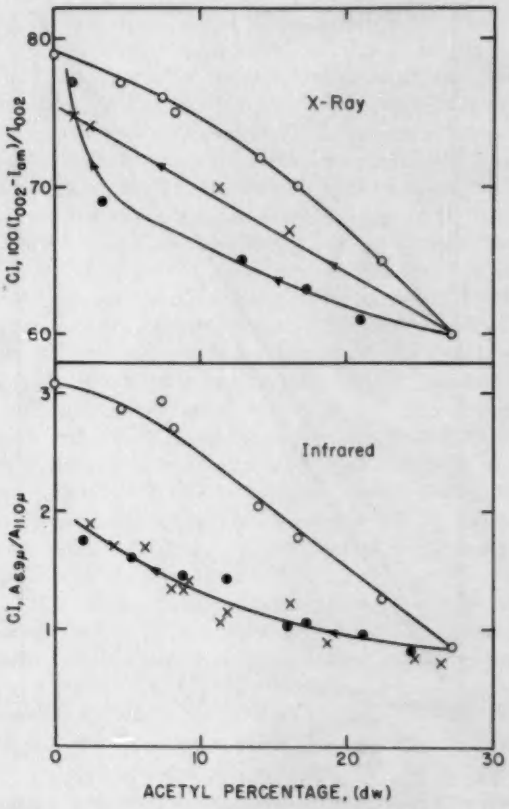

Fig. 6. Percentage acetyl (dw) vs. crystallinity index as determined from x-ray and infrared measurements. ○, original PA cottons; ●, after deacetylation of Sample 7 by 2 *N* HCl; ×, after deacetylation of Sample 7 by *N*/2 NaOH.

Density Measurements

Acetylation. The relationship between density and acetyl percentage on a dry weight basis was established by Orr et al. [13] from measurements on a large number of PA cottons including the present samples. Using these data, V_1, the volume to which 1 cc. of cotton cellulose changes on acetylation, was calculated for various degrees of acetylation and was plotted against percent acetyl (ahg), as shown by the lower curve in Figure 7. The values at the higher acetyl percentages form a straight line which, when extended (dotted line), passes through the origin. At lower acetyl percentages, between 0% and about 20% acetyl, the curve forms a definite

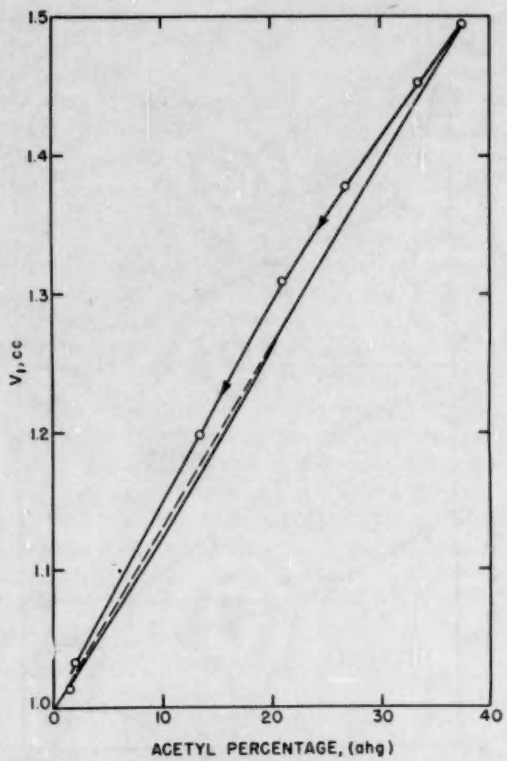

Fig. 7. Calculated volume of 1 cc. of cotton cellulose at various degrees of acetylation. Lower curve from density data of Orr et al. [13]; upper curve from density data for Sample 7 after partial deacetylation.

bulge below the dotted line, so that the volume is less than that of the linear relationship established in the higher acetylation range. The maximum deviation is in the vicinity of 10% acetyl; i.e., close to the percentage representing the triacetylation of all the amorphous.

A number of interesting conclusions can be drawn from this acetylation curve, since its slope at any point shows the rate at which a 1-cc. sample of cotton increases in volume as the acetyl percentage is increased. The rate is constant (0.0132 cc./% acetyl) from about 20% to 37.4%, and this is the same as the average rate between 0 and 37.4%, represented by the slope of the straight line through the origin. At the lowest acetyl percentages, the observed rate is less than the average and gradually increases to equal the average in the vicinity of 10% acetyl. Between about 10 and 20%, the rate increases still further and finally decreases to equal the average rate again at about 20%. Thus, starting with a given volume (or weight) of cotton cellulose, the volume increase accompanying the introduction of an additional percentage of acetyl is relatively low at lower acetyl contents, increases to a maximum, and finally decreases to a constant value at higher acetyl contents.

This curve is reasonable in the light of the accepted microstructure of cotton; the crystallites have a definite specific volume, and the specific volume in the amorphous regions is not at all uniform. The first acetyls may enter the most accessible portions of the amorphous regions, so that the cellulose volume is increased comparatively little. The more acetyl groups added, the greater must be the spread in the amorphous region to accommodate these bulky groups. Eventually, a degree of substitution is reached beyond which the acetyl groups can no longer be accommodated by modification of the amorphous volume alone, and the cellulose chains entering the crystalline regions are spread apart; during this stage, the overall volume of the cellulose increases more rapidly. Finally, with the introduction of acetyls into that portion which was originally crystalline, a steady increase in volume ensues as the crystalline region alone expands to accommodate the groups.

Another conclusion which can be drawn from the acetylation curve is the fact that the conversion of amorphous to acetylated amorphous cellulose involves a smaller change in V_1 than the conversion of an equal amount of crystalline to acetylated crystalline cellulose. The average rate from 0 to 13.6% is about 0.0125 cc./% acetyl as compared with the average rate of 0.0138 cc./% acetyl from 13.6 to 37.4% for the crystalline acetylation.

It can be concluded from evidence already presented that acetylated amorphous cellulose has a lower degree of lateral order and therefore, by implication, a higher specific volume than acetylated crystalline cellulose. This follows from the findings that acetylated amorphous cellulose has the higher iodine sorption capacity, is attacked selectively by hydrochloric acid, and forms a less crystalline cellulose when deacetylated.

Deacetylation. When the 37.4% acetyl sample is deacetylated by hydrochloric acid, the change in V_1 (as calculated from density measurements) follows the upper curve in Figure 7. The exact contour of the curve has not been established, since only a lim-

ited number of density determinations was made. It is apparent, however, that the value of V_1 for a deacetylated sample is always greater than that for the sample having the same acetyl content on the acetylation curve; i.e., a given volume of cotton cellulose brought to 37.4% acetyl and subsequently deacetylated has a greater volume than a sample acetylated directly to the same final acetyl percentage.

The fact that there is a marked change in the slope of the deacetylation curve at about 21% acetyl, close to the point (23.7%) where all the acetylated amorphous has been deacetylated, tends to confirm the conclusion that the acetylated amorphous cellulose is deacetylated first. A comparison of the slopes below and above the break would therefore indicate that the deacetylation of acetylated crystalline cellulose involves a greater decrease in volume than the deacetylation of acetylated amorphous cellulose.

It can also be concluded from Figure 7 that the specific volume of the amorphous cellulose formed by deacetylation of the acetylated amorphous is slightly larger than that of the original amorphous. This follows from the fact that the increase in V_1 caused by the addition of the first 13.6% acetyl on the acetylation curve is about 0.0170 cc., while the corresponding decrease resulting from the removal of the first 13.6% acetyl from the 37.4% acetyl sample is only 0.0159 cc. Assuming the same volume for the acetylated amorphous in both instances, the amorphous cellulose must occupy a greater volume in its "restored" state. This is consistent with the finding that restored amorphous has a higher moisture sorption capacity than the original amorphous cellulose.

General Discussion

In any theoretical analysis of the property changes which take place when cotton is partially acetylated or when a PA cotton is partially deacetylated, cognizance must be taken of the nature of the inhomogeneous volume changes within the fiber. On acetylation, the amorphous cellulose, which constitutes 17% of the cotton studied, is considered to be completely converted to the triacetate at an acetyl content of 13.6%. From the density data and the change in weight involved, it can be shown that there is a 17% increase in volume when the cotton is acetylated to this extent. Since the crystalline cellulose is not appreciably affected, this volume increase can be attributed entirely to the increase in volume of the amorphous regions; that is, the amorphous cellulose must now occupy about twice its original volume.

According to the accepted theory as to the fine structure of cotton cellulose, each macromolecule passes through several crystallites and the intervening amorphous regions. Thus, the crystallites will not behave as separate discrete entities, since they are interconnected by a network consisting of those portions of the macromolecules passing through the amorphous regions. The preferential increase in volume of the amorphous region by its triacetylation must result in the development of tremendous stresses within the fiber which tend, on the one hand, to increase the volume of the fiber and, on the other hand, to restrict the volume increase. Acetylation beyond this point would result in the acetylation and the increase in volume of the outer layers of the crystallites with the consequent development of stresses at the edges of the unattacked crystalline areas and modification of the stresses in the acetylated amorphous regions.

Other stress patterns would develop during the deacetylation of a highly acetylated PA cotton. These in turn would differ depending upon whether deacetylation was effected by hydrochloric acid or by sodium hydroxide, because of the difference in the topical volume changes taking place within the fiber in the two instances. The degree of lateral order in the deacetylated cellulose formed can be expected to differ accordingly.

When Sample 7 (37.4% acetyl) is subjected to hydrochloric acid hydrolysis, the loss in volume during the removal of the first 13.6% acetyl can theoretically be attributed entirely to the conversion of the acetylated amorphous regions to the unacetylated state. The crystallites are still swollen, however, and therefore tend to prevent the restoration of the amorphous regions to their volume in the original cotton, where the crystallites are unswollen. In other words, the restored amorphous would have a more open structure or a lower degree of lateral order than the original amorphous. This is in harmony with the conclusion, drawn from the density data, that the increase in V_1 on adding the first 13.6% acetyl to the cotton is about 5% greater than the decrease on removing the first 13.6% acetyl from Sample 7. It would also explain the fact that the moisture sorption capacity of the restored amorphous was found to be greater than that of the original amorphous.

A different degree of lateral order would be expected after deacetylation of the 37.4% acetyl sample by sodium hydroxide, since here the acetylated amorphous and crystalline regions are deacetylated at the same time, with little or no selectivity. In this instance, the acetylated amorphous and crystalline regions are decreasing in volume simultaneously, so that a higher degree of order would be anticipated than after hydrochloric acid deacetylation. This explains the fact that the moisture sorption curves for the samples deacetylated by sodium hydroxide fall below the corresponding curves for hydrochloric acid (Figure 5). It is also in harmony with the x-ray crystallinity index data, which indicate that a larger amount of crystalline cellulose forms when deacetylation is carried out by sodium hydroxide.

The results substantiate the fact that acetylated cottons of a given acetyl content may differ widely in their properties, depending upon whether the acetyl content is arrived at by direct acetylation of the cotton or by acetylation to a higher degree and subsequent deacetylation. If the latter method is used, the properties will depend further upon whether hydrochloric acid or sodium hydroxide is used for deacetylation and also upon the original acetyl content before deacetylation. To illustrate the magnitude of the differences involved, interpolated values for various properties have been listed for five acetylated cottons having an acetyl content of 13.6% (ahg), each prepared in a different way (Table II).

Theoretically, all the acetyl in Sample I would be in the form of acetylated amorphous, and no unacetylated amorphous cellulose would be present. In Sample II, the amorphous would have been restored, and all the acetyl would be in the form of acetylated crystalline cellulose. Thus, in Sample I, only the amorphous regions of the original cotton would have been expanded by acetylation and, in Sample II, only the crystallites. Sample III would presumably differ from Sample II by the presence of additional deacetylated cellulose surrounding the expanded crystallites.

The fibers of Sample IV can be pictured as consisting of a core containing crystalline, acetylated crystalline, and acetylated amorphous cellulose enclosed in a completely deacetylated sheath. The cellulose in this outer layer would be expected to have a different degree of lateral order from that of ordinary cotton cellulose, since it would be stretched around a core having a volume about 35% greater than in the original cotton fiber. Sample V would resemble IV in structure, but its core would be smaller and less dense.

TABLE II. Comparison of Properties of Various PA and Deacetylated PA Cottons Having an Acetyl Content of 13.6% (ahg)

	Method of preparing the 13.6% acetyl sample	ISV*	Moisture sorption† %	Crystallinity index (x-ray)	Crystallinity index (Infrared)	Density, g./cc.	V_1 cc.	Constituents‡
I	Direct acetylation	111	4.4	73	2.3	1.49^8	1.17^0	C AA
II	Deacetylation with HCl from 27.2% acetyl	111	7.6	—	—	—	—	C A AC
III	Deacetylation with HCl from 37.4% acetyl	133	8.6	64	1–1.3	1.46^4	1.20^5	C A AC
IV	Deacetylation with NaOH from 27.2% acetyl	125	6.4	—	—	—	—	C A AA AC
V	Deacetylation with NaOH from 37.4% acetyl	144	6.6	70	1–1.3	—	—	C A AA AC

* In mg. iodine per g. anhydroglucose residue.

† In g. water per 100 g. anhydroglucose residue.

‡ C = crystalline cellulose; AA = acetylated amorphous cellulose; A = amorphous cellulose; AC = acetylated crystalline cellulose.

The differences in the properties of these five samples can therefore be attributed to differences in the proportions and distribution of the various constituents within the fiber and to the differences in fine structure and stress patterns resulting from inhomogeneous volume changes.

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The Fate of Thioglycollic Acid in Wool Durably Creased with Thioglycollate

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Abstract

The fate of thioglycollic acid in wool fabrics durably creased with ammonium thioglycollate was investigated. The effect of various treatments was followed by means of S^{35}-labelled thioglycollate, which was added to the ammonium thioglycollate solution used in imparting a crease. It is shown that steam ironing is not associated with loss of labelled thioglycollate, whereas washing with water results in rapid loss of radioactivity, followed by a much slower decrease. Almost complete loss of radioactivity can be brought about by treatment with sulfide, sulfite, or alkaline cyanide, whereas lithium bromide or urea has little effect. It is concluded that of the 4–9 mg. thioglycollate initially applied per gram of wool, 3–5 mg. are in a labile but nonvolatile state, whereas the remaining 1–4 mg. are probably in a mixed disulfide form. At the most this represents 4 or 8% of the half-cystine residues available in wool as the mixed disulfide. The findings are discussed in the light of current theories of permanent setting.

Introduction

In the recently developed Si-Ro-Set process [1, 2], a neutral solution of ammonium thioglycollate is applied to a wool fabric, and a durable crease is then imparted by holding it in a steam press for a short period. Earlier work by Farnworth [4] leading to the development of this process suggested that the mechanism of the reaction could be explained by the breakdown of hydrogen bonds and their reformation following scission of some cystine linkages.

It was considered of interest to study various aspects of the reaction and if possible to elucidate the reaction mechanism further with the aid of S^{35}-thioglycollic acid.

Materials and Methods

Woolen Fabric

A standard cloth (Serge 745), manufactured by Yarra Falls Pty. Ltd., Melbourne was used throughout.

S^{35}-Thioglycollic Acid

The labelled thioglycollic acid (initially containing 7.2 mc. in 91.5 mg.) was obtained from the Radiochemical Centre, Amersham, U. K. A stock solution was prepared by diluting to 100 ml.; this solution was then stored in the deep-freeze and aliquots thawed out as needed.

Durable Creasing

A 4% (vol./vol.) solution of ammonium thioglycollate at pH 7 containing 0.2% (vol./vol.) Alkarene (Polymer Corporation Pty. Ltd., Sydney) was prepared. The radioactive Si-Ro-Set solution was a 1:1 mixture of the ammonium thioglycollate and stock S^{35}-thioglycollate solutions.

The solution was applied as uniformly as possible with a 1-in. paint brush on pieces of fabric. It was found that a 5-ml. solution was generally sufficient for 100–150 $cm.^2$ of fabric; of this the brush retained almost 4 ml., leaving only 1 ml. to be actually applied. The fabric was folded in half and a crease was imparted by exposure to steam and pressure for 20 sec., followed by dry heat for 30 sec. A steam iron fitted with a false bottom was used in place of the steam press recommended in the commercial (Si-Ro-Set) process [1, 2].

Ironing was carried out by two methods. In Method 1 the fabric was placed on a filter paper and covered with several thicknesses of cheesecloth prior to ironing, while in Method 2 the fabric was placed on a metal sheet and ironed directly.

Sampling Technique

Samples of 1 cm.², weighing 20 mg., were punched out of the treated fabrics nonselectively, avoiding the crease and edges.

Washing Procedure

Treated fabric was wrapped in copper gauze and left under running tap water for varying periods of up to two weeks.

Conversion of Organic Sulfur to Barium Sulfate

The method of Walkenstein and Knebel [11] was used on a one-tenth scale for 20-mg. samples of fabric and on 20μl. radioactive Si-Ro-Set solution. To ensure a suitable count, it was found necessary to add 3 ml. 0.1 *N* sulfuric acid as carrier sulfate in each case.

Counting Technique

All counting was done on 1 cm.² aluminum planchets, using a thin end-window Geiger-Müller tube (EHM 2⁸) with a conventional scaler unit. Samples of fabric and barium sulfate were counted at infinite thickness. Where necessary, fabric samples were brought to constant weight by addition of water to eliminate dilution effects. A standard error of counting of ±5% or less was generally adhered to. Correction for decay was applied when necessary.

Results

Effect of Steam Ironing

The two methods of ironing were examined to determine which resulted in the more uniform distribution of the label over the fabric. Two fabrics were treated by each procedure. Six samples from each of these fabrics were then counted and estimates of variance (within fabrics) obtained; these were 5.73 and 209.78 for Methods 1 and 2 respectively. The variance of Method 2 was significantly greater ($P < 0.001$) than that of Method 1. The distribution of radioactivity was thus more uniform with Method 1, and in subsequent work only this method of ironing was used.

It was considered of interest to determine whether or not ironing resulted in loss of thioglycollate through volatilization. In these experiments, three samples from each of two labelled fabrics were used to test the effect of the treatment. Each sample was counted both before and after ironing; the results were analyzed statistically. The reduction in counts/min. due to the ironing was 18 with a standard error of ±14 and is thus not significant.

Effect of Water Washing

As shown in Figure 1, the radioactivity of a fabric dropped rapidly with washing for the first 16–40 hr., after which time a much slower loss of radioactivity was observed. The slower phase is a little in excess of the loss expected if only radioactive decay were operative and is therefore due to a slow leaching-out process. The unwashed fabric, on the other hand, lost radioactivity at a rate comparable with the anticipated decay, thus indicating no volatilization of the reagent on standing in air. A similar result was obtained with a second fabric.

It is significant that, in spite of the loss of radioactivity associated with washing, there was no sign of the crease being affected. Nevertheless, parts of

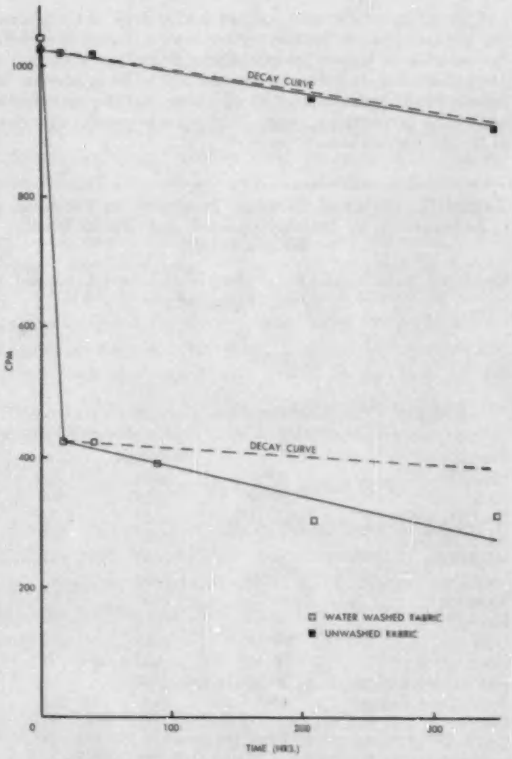

Fig. 1. Effect of storing in air and washing in water on the retention of radioactivity by durably creased woolen fabric. (Means of three washed and unwashed samples of Fabric IV are plotted, together with the theoretical decay curves expected from the 0 and 16 hr. washed samples.)

the fabric which had been ironed flat in the initial treatment wrinkled even after short immersion in water.

The amount of radioactivity associated with two fabrics at various stages of washing was calculated in terms of thioglycollic acid content and is presented in Table I. Figures obtained by direct counting are in good agreement with those obtained following conversion to barium sulfate. From these results it appears that the content drops from about 4–9 mg. thioglycollic acid per gram of wool to about 1–4 mg. in the early stages of washing.

TABLE I. Effect of Water Washing on Thioglycollic Acid Content of Durably Creased Woolen Fabrics

Fabric no.	Hr. washing	Thioglycollic acid content of wool in mg./g.* from $BaSO_4$ count	from direct count
III	0	3.7	3.7
	40	1.1	1.4
IV	0	8.7	8.7
	40	3.7	3.6
	350	2.7	3.0

* The thioglycollic acid content was arrived at by comparing the count of the barium sulfate from a radioactive Si-Ro-Set solution of known thioglycollic acid content with that of the barium sulfate from the test sample. The figures for the direct count were calculated by assuming that the count before washing is proportional to the thioglycollate content as arrived at by the barium sulfate method.

TABLE II. Effect of Chemical Treatment on Retention of Radioactivity by Durably Creased and Water Washed Woolen Fabric

Duplicate 1-cm.² samples of Fabric IV were immersed in 10 ml. of reagent.

Reagent	Concentration	Conditions	% Drop in radioactivity after treatment*
Water	—	hot/cold	0
Na_2CO_3	10%	cold	29
NH_3	27%	cold	28
Na_2CO_3:KCN	10%:10%	cold	97
NH_3:HCN	†	cold	97
Na_2S:CO_2	‡	cold	97
Na_2SO_3	10%	cold	85
$NaHSO_3$	10%	cold	72
$Na_2S_2O_5$	10%	cold	79
LiBr	10 *M*	cold	22
Urea	8 *M*	cold	0
Sod. thioglycollate	10%	cold	12
Sod. thioglycollate	10%	hot	91

* This was calculated from the mean of two samples from $\frac{\text{count before treatment} - \text{count after treatment}}{\text{count before treatment} - \text{background}} \times 100$.

† HCN was generated from 10 g. KCN and bubbled through 10 ml. 27% NH_3 (sp. gr. 0.88).

‡ CO_2 was bubbled through 10% Na_2S until the pH dropped to 8.5.

The observed variations could be due to different extents of penetration of the reagent. It is noteworthy that penetration is incomplete under the conditions described, as shown by the fact that the count of the reverse side is at times only 10% of the treated side. The figures presented here are not to be taken as minimal, since no attempt was made to determine the lower limits of thioglycollate initially required to give a durable crease. The amount of thioglycollate applied is of the same order of magnitude as that recommended by Farnworth [5].

Effect of Various Chemical Treatments

Fabric IV, which had been exhaustively washed with water to dispose of all the readily removable radioactivity, was treated for 1 hr. in the cold or 10 min. in a boiling water-bath with reagents listed in Table II, then rinsed for 15 min. in tap water prior to counting.

It is clear that the hydrogen bond breakers, urea and lithium bromide, had little or no effect on the radioactivity of the fabric. Similarly, cold thioglycollic acid did not appreciably exchange, thus ruling out physical adsorption by the fabric. Alkali has only a small effect, whereas sulfide, alkaline cyanide, and hot thioglycollate result in loss of the bulk of the radioactivity. Sulfite, bisulfite, and metabisulfite also removed much of the radioactivity.

Particular importance is attached to the fact that none of the cold treatments resulted in loss of the crease imparted by the durable creasing treatment, even when all the radioactivity was removed. This suggests that the presence of thioglycollic acid is not required for crease retention.

Discussion

Evidence regarding the nonvolatility of thioglycollate during steam ironing confirms the earlier observation by Farnworth [5] that ammonium thioglycollate is nonvolatile on steam distillation. It is clear, however, that a portion at least of the thioglycollate is in a labile but nonvolatile form and is easily displaced from one part of the fabric to another when exposed to a jet of live steam (Ironing Method 2). It is thought possible that this labile

form of thioglycollate may correspond to the portion most easily washed out with water (Table I and Figure 1).

It is suggested that the labile form may represent free thioglycollate and/or dithiodiglycollate, whereas the bound portion may be present in the form of a mixed disulfide, as would appear from results of chemical treatments (Table II). Such a mixed disulfide could arise by exchange of a half-cystine for thioglycollate by a mechanism envisaged by Kolthoff, Stricks, and Kapoor [7] and Eldjarn and Pihl [3], as represented by

$$\mathrm{CySSCy} + \mathrm{TSH} \rightleftharpoons \mathrm{CySST} + \mathrm{CySH} \qquad (1)$$

where CySSCy stands for cystine and TSH for thioglycollic acid. This reaction may be followed by an oxidative step giving further mixed disulfide

$$\mathrm{CySH} + \mathrm{TSH} + \mathrm{O} \rightarrow \mathrm{CySST} + \mathrm{H_2O} \qquad (2)$$

Since wool contains about 0.30% by weight or 30μ moles/g. cysteine [6], some thioglycollate could be incorporated into the mixed disulfide by Step 2 alone.

If the "cystine" (cystine + cysteine) content of wool is taken as 12% by weight or 500μmoles/g., and assuming an overall reaction (1)+(2)

$$\mathrm{CySSCy} + 2\mathrm{TSH} + \mathrm{O} \rightarrow 2\mathrm{CySST} + \mathrm{H_2O} \qquad (3)$$

then the maximum amount of thioglycollate which could be bound in mixed disulfide form is theoretically 1000μ moles or 92 mg./g. of wool. For Equation 1 alone the maximum binding is 46 mg. thioglycollic acid per gram of wool. It is evident that under present conditions (Table I) up to 8% of the cystine cross-links could be implicated in the binding of thioglycollate by assuming Equation 1, or no more than 4% according to Equation 3.

It can also be calculated that the maximum amount of cystine residues that could theoretically be reduced to cysteine by the available thioglycollate (Table I) assuming the reaction

$$\mathrm{CySSCy} + 2\mathrm{TSH} \rightleftharpoons 2\mathrm{CySH} + \mathrm{TSST} \qquad (4)$$

is about 4.0 and 9.5% for fabrics III and IV respectively.

Farnworth [1, 4] postulates that the function of the thioglycollate in the Si-Ro-Set process is to reduce cystine disulfide bonds. The wool is made accessible to water, which in turn causes hydrogen bond breakage. The set is then imparted by a rearrangement of the hydrogen bonds. This explanation has been put forward in place of earlier theories of setting [8, 9, 10], which involve a hydrolytic first step

$$\mathrm{CySSCy} + \mathrm{H_2O} \rightleftharpoons \mathrm{CySH} + \mathrm{CySOH} \qquad (5)$$

followed by cross-link formations of various kinds. The incorporation of thioglycollic acid into the wool protein in form of a mixed disulfide could equally well be explained on either a reductive or hydrolytic first step; in the latter case either by Reaction 2 following Reaction 5, or, in absence of oxygen, by a reaction involving the sulfenic acid

$$\mathrm{CySOH} + \mathrm{TSH} \rightleftharpoons \mathrm{CySST} + \mathrm{H_2O} \qquad (6)$$

It is thus concluded that the results presented in this paper do not conflict with the reaction mechanism postulated by Farnworth. However, no further evidence against the alternative theory has been provided.

Conclusions

When applied to woolen fabrics by a process similar to the Si-Ro-Set process, thioglycollate is retained on steam ironing, washed out in part with water without loss of crease, and almost completely removed by sulfide, sulfite, and alkaline cyanide (but not by urea or lithium bromide) in the cold, also without loss of crease. The thioglycollate is probably present in a free (possibly as dithiodiglycollate) and mixed disulfide form in the treated fabric. Less than 8% of the total half-cystine + cysteine residues of the wool are involved in the mixed disulfide formation. The thioglycollate plays no part in the retention of the crease.

Acknowledgments

I wish to thank Dr. A. J. Farnworth for helpful criticism and for making his unpublished observations available to me; also Dr. J. M. Swan for valuable discussion and Mr. W. B. Hall for statistical analysis.

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Change of Cross-Sectional Area of Single Jute Filaments with Relative Humidity

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Introduction

An important effect of moisture absorption by natural bast fibers like jute is swelling. The maximum swelling of jute at saturated moisture content, measured directly or indirectly, was studied earlier [2, 5], but there had been no attempt to study the swelling of individual jute filaments at different successive values of relative humidity. This article is a report of some work that was done on the subject by the author.

The cross sections of single jute filaments are very irregular; this makes them poor subjects for microscopic measurements [9]. For this reason, conclusions drawn from the results are only qualitative. Calculations of cross-sectional area were based on measurements of transverse widths of the filaments at two directions mutually at right angles. Air of the required relative humidity was obtained by passing it through a series of bottles containing solutions of sulfuric acid [12]. Studies were principally made on samples of raw (untreated) jute. A few samples of jute from which hemicellulose and lignin had been removed separately were also tested for comparative study; the results are presented graphically.

Experimental Procedure

The centerpiece of the apparatus used was a rectangular plastic chamber C (Figure 1) with an air-tight glass plate lid P. Two glass tubes T formed the inlet and outlet for the air circulating through the chamber. Two pieces of plastic strips SS were so fixed that they held the filament carriers FC, made of brass wire, parallel to one another. Each carrier had a bow-spring CW of thin enameled copper wire, fixed at its center to hold the jute filament F with a slight tension to keep it taut. One of the plastic strips holding the filament carriers had six brass wire arrestors AA suitably placed. The carriers, secured loosely in their holders and with filaments mounted on them, could be made to rest in either of the two mutually orthogonal positions by manipulating the chamber as a whole. This will be clear from Figure 2.

Though it had recently been found that the sorption equilibrium of single jute filaments was usually attained within a few minutes [11], in the present experiment air of the required RH was passed continuously for 24 hr. at approximately a constant rate before each observation. The chamber was rigidly clamped, and measurements were made on successive filaments by bodily moving the microscope and viewing by transmitted light through a black paper grating G pasted over the glass lid of the chamber. The reticule in the eyepiece with the magnification used made it possible to measure the transverse widths with an accuracy up to 3.30×10^{-4} cm.

For each sample, 25 filaments in 5 sets of 5 filaments each were tested. Each filament was meas-

ured, along its length, at five successive points each 1 mm. apart, in one position of the filament carrier. The mean value of the cross-sectional area was obtained as proportional to the product of the two mean crosswidths obtained from $5 \times 5 \times 5 = 125$ readings for each angle of measurement (0° and 90°). The resultant Standard Error varied between 3 and 7%, which is generally the range in almost all dimensional measurements of jute filaments by such methods.

The following RH's were used: 0, 10, 25, 35, 50, 60, 75, 85, 95, and 100%. For 0% RH two bottles containing concentrated H_2SO_4 were followed by a $CaCl_2$ (fused) tower before being connected to the chamber. Distilled water was used for 100% RH. Temperature of the room varied between 21° C. and 27° C.

Results and Discussion

Filaments of one tossa jute (*Corchorus Olitorius*) and of one white jute (*Corchorus Capsularis*) were tested over five cycles of relative humidity. No systematic variation could be observed. According to White and Eyring [11], repetition of cyclic sorption history in cotton, another natural cellulosic fiber, also produced identical isotherms.

Observations were then made to discover any hysteresis effect in cross-sectional swelling during absorption and desorption processes. The result is shown in Figure 3, along with a typical sorption isothermal for samples of jute. Such a close resemblance of the two in the case of cotton was found by Collins [1] long ago. But in this case of jute, a few points of difference appear to be interesting. The extent of hysteresis at the higher values of RH is more prominent in cross-sectional swelling than in moisture sorption process. Moreover, the point of inflexion at low humidity is almost absent in the swelling curve, which shows practically no hysteresis up to 25% RH. Taking thin cross sections of different fibers, Morehead [3] also observed the absence of any definite point of inflexion at the lower humidities. It may be that the sorption of moisture at low humidities is shared by the pores in the fiber as well as the fiber substance itself. The moisture taken up by the pores does not contribute to swelling until they are filled up. Thus swelling lags behind moisture regain in the initial stages. This is Pierce's well-known two-phase theory of moisture sorption. However, a reversal of this state of affairs at the higher humidities calls for probable explanation. Stamm and Tarkow [10] maintain that the total amount of liquid lost or taken up by a cellulosic material on drying or soaking is not a gauze of liquid leaving or penetrating the fiber substance. In addi-

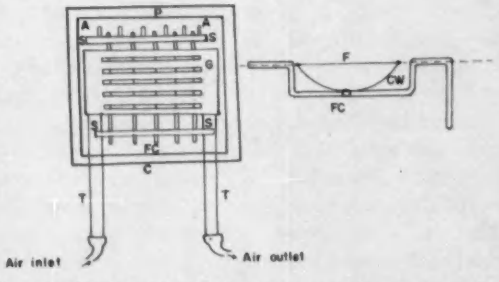

Fig. 1. Airtight plastic chamber containing mounted jute filaments; filament carrier shown alongside.

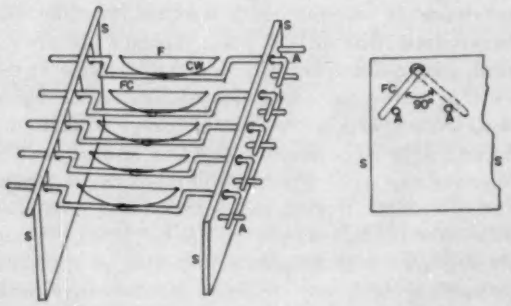

Fig. 2. Details of mounting of jute filaments in carriers and holding them for measurement of cross-widths at two mutually perpendicular directions.

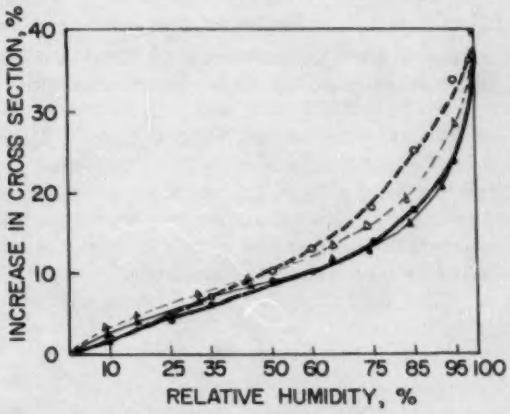

Fig. 3. Hysteresis in cross-sectional swelling of jute filaments (thick line) and moisture regain hysteresis of jute (thin line). Full line indicates absorption and dotted line, desorption.

tion to the normally rigid capillaries, "transient capillaries" approaching molecular dimensions may play an important part at higher humidities. During absorption some of these transient capillaries may coalesce to form rigid pores or add to those already present, which would result in an increase in the overall dimension of the fiber cross section. Therefore, the cross-sectional swelling may not follow the desorption isothermal, and the hysteresis in the former may be more than that in moisture regain.

Curves (not shown) for jute from which major portions of hemicelluloses and lignin were removed separately by alkali treatment [7] and bleaching [6] were essentially similar to that for raw jute. Hemicelluloses when isolated are highly hygroscopic, and it is this substance that is believed to be largely responsible for the hygroscopicity of jute. Thus alkali treated jute is expected to show a marked difference in sorption and resultant swelling behavior from that of raw jute. Though not prominent, such a difference was clearly discernible in the swelling curve for alkali treated jute. The curve flattened out over a considerable range of RH just beyond 25% RH. Ramaswami and Mukherjee [4] observed an overall depression in the moisture regain curve of alkali treated jute. Separated lignin has little affinity for water; naturally, bleached jute showed very little difference from that of raw jute in swelling behavior. This is in conformity with Sen and Hermans [8], who found inappreciable change in swelling behavior of jute on delignification up to 0.5% lignin.

Summary

Change in cross-sectional area determined by cross-width measurements of single jute filaments as a result of sorption of moisture closely resembles the moisture regain isothermal. Hysteresis is prominent only at higher values of RH, and the small differences between the two curves had been explained by Pierce's two-phase theory of moisture sorption supplemented by the hypothesis of "transient capillaries" coalescing to form additional rigid pores during absorption. Removal of hemicelluloses depresses overall swelling of jute, with slower rate of change over the middle ranges of RH. Delignified jute exhibits almost the same characteristic as raw jute.

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A Wear Study of the Serviceability of a Minimum Care Garment

Part I: Subjective Evaluation

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Abstract

The serviceability of a minimum care type garment was studied. Men's slacks made from 65% Dacron [2] and 35% rayon fabric were worn a total of 750 hours. After every 150 hours of wear, half of these garments were drycleaned and half home laundered. The garments were evaluated by both the wearers and members of the research staff after each wear period and after each cleaning.

The slacks were found to be generally serviceable after wear and cleaning. The drycleaned and pressed garments were consistently rated as having a better appearance than the laundered and pressed garments. It was necessary to press the laundered slacks before they were acceptable for wear.

GARMENTS designed to require a minimum amount of care are one of the recent developments in the textile and clothing field. These garments, advertised as "wash and wear" or minimum care items, maintain an overall appearance similar to their original condition when laundered by home methods. They are said to require little or no pressing, since wrinkles are removed and pleats and creases are retained during laundering. These properties are among those listed by Rawlings et al. [2] for properly prepared "wash and wear" garments of hydrophobic fibers.

Such ease of care properties and the low cost of maintenance have considerable appeal to consumers; however, some minimum care garments when laundered at home have fallen short of the consumer's expectations because of poor serviceability. A serviceable garment should not only be durable, but should maintain a satisfactory appearance during wear. Since garments that formerly required drycleaning are now being manufactured from minimum care fabrics, it is reasonable to assume that some consumers may expect such garments, when home laundered, to meet the appearance standards set by professionally cleaned and pressed garments. Appearance standards are also affected by the fastidiousness of each wearer and with the occasion and place a garment is to be worn.

Despite the increased volume of minimum care apparel on the market, few studies have been reported concerning their serviceability or the effectiveness of different methods of maintenance on such garments. Therefore, a wear study was undertaken to determine the effects of home laundering and commercial drycleaning on the serviceability of a typical minimum care garment. As a measure of serviceability, garment appearance after wear and cleaning, as well as fabric durability, was studied. "Wash and wear" men's slacks made of blended Dacron/rayon gabardine were selected for the investigation. In this paper the subjective evaluation of the garments, by both the wearers and textile laboratory staff, is reported. Since little published information is available concerning wear study methods, the technique employed in conducting this study is described. A later paper will present the results of a laboratory evaluation of the garments.

Procedure

The blended fabric of 65% Dacron staple (3 den./fil.) and 35% rayon staple used in this study is described in Table I. All slacks were made from the same lot of fabric by a quality manufacturer; the approximate retail price was $15. Information con-

[1] California Agricultural Experiment Station.

[2] Du Pont trademark.

TABLE I. Descriptive Properties of Fabric and Yarn

Fabric properties		Yarn properties	
Fiber content, %	Dacron 68.07 Viscose rayon 31.93	Direction of twist	Warp and filling: Z/S, S/Z
Finish	Urea formaldehyde		
Weave	2/1 twill	Number (560 yd./lb.)	
Yarns/in.	94 × 46	warp: ply	16.90
		filling: ply	16.79
Wt, oz./sq. yd.	9.30	Twist/in. of yarn	
		warp: ply	20.4
		singles	20.3
Thickness, in.-1.0 p.s.i.	0.025	filling: ply	19.2
		singles	19.1
Strength, lb.		Strength, G.	
warp: dry	152	warp	633
wet	159	filling	693
filling: dry	78		
wet	81	Elongation, %	
Elongation, %		warp	39
warp: dry	85	filling	35
wet	93		
filling: dry	55		
wet	59		

tained on the hangtag described the garments as "wash and wear" and stated that the garments were machine washable, required little or no ironing, and retained a permanent press after washing. Laundering instructions on this tag called for moderately hot wash water, pretreatment of heavily soiled areas, and drip drying. The slacks were tailored in the conventional manner, and the construction and findings were generally compatible with the minimum care properties of the fabric. The seams were sewn with 3-ply mercerized cotton thread with 12 stitches per inch.

All male staff members in three departments of the University of California were invited to participate in the wear study. The men in these departments did office type work and would not normally come in contact with heavy soil. The first 25 men responding became subjects in the study, and were issued two identical garments. The men selected ranged from approximately 25 to 45 years in age, and wore from size 28 to 42 garments.

The men were instructed to wear each pair of slacks at least twice a week, alternating the two garments, until each pair had been worn 150 hr. (±5 hr.). They were asked to treat both garments in as similar a manner as possible, not to press the slacks, to keep the garments on pants hangers when not being worn, and not to attempt to remove spots from the slacks themselves.

A questionnaire was issued to each wearer, to be completed and returned at the end of each wear period. The wearers were asked to evaluate both garments for: (1) crease retention, shape retention, and wrinkle resistance, by selecting a descriptive term from a list ranging from "excellent" to "unacceptable"; (2) fabric surface changes by reporting if fuzz or pills were observed; (3) fabric hand by selecting the "softest" garment if a difference was noted; and (4) overall preference.

One of the garments issued to each wearer was laundered and the other was drycleaned. However, the wearers were not aware of the maintenance methods being used on their slacks. The garments were returned to the laboratory for cleaning, staff evaluation, and measurement for dimensional change, after 150, 300, 450, 600, and 750 hr. of wear. Ten garments were withheld at the end of each wear period for physical analysis.

The slacks were visually rated in the laboratory by three textile research staff members according to the following rating scale:

Rating 1.0—No change from original appearance
Rating 2.0—Slight change from original appearance
Rating 3.0—Moderate change from original appearance
Rating 4.0—Unacceptable appearance
Rating 5.0—Unwearable condition

The items subjectively rated after wear and before cleaning were front crease retention, shape retention, wrinkling, pilling, fuzz level, lint pickup, and abrasion. The differences among the individual staff ratings given the paired garments were analyzed for statistically significant differences using the Wilcoxon Matched-Pairs Signed-Ranks test [4]. The garments were also evaluated by the staff after cleaning at each wear level for front crease retention, shape retention, wrinkling, and seam puckering. The laundered garments were evaluated after washing and again after pressing; drycleaned garments were evaluated only after commercial drycleaning plus pressing.

Laundering was done in the research laboratory in a manner similar to that described by Rawlings et al. [2] for "wash and wear" garments of hydrophobic fibers. An automatic agitator type home washing machine was used. Heavily soiled areas were prespotted before laundering with a neutral soap paste or carbon tetrachloride, depending on the nature of the soil. Water of zero degrees hardness, softened with an ion-exchange type softener, and a 0.002% solution of neutral chip soap, Federal Specification P-S 566, were used. A 4-lb. load was soaked for 1½ min., washed for 4½ min. at 110° F. (±2°), rinsed for 10½ min. with an overflow type rinse at 70° F., and extracted for 7½ min. by centrifugal action at 650 r.p.m. The garments were tumble dried in an electric condenser-type household dryer at 175° F. (±5°) for 25 min., followed by a 5-min. tumbling with the heating current shut off. The slacks were removed immediately from the dryer and hung by the cuffs until completely dry. After staff evaluation for appearance after laundering, the slacks were pressed with a home-type steam iron. All slacks were pressed by the same technician throughout the study. Ten to fifteen minutes were required to press the entire garment, with special emphasis on creases, seams, and cuffs.

All garments were drycleaned at a commercial plant. The experimental garments were added to the normal work load of the plant and received no special treatment. The cleaning procedure included a 25-min. run in 4% charged Stoddard solvent, 75% RH; a 4-min. extraction; a 5-min. rinse in clear solvent; a 4-min. extraction; and tumble drying at 120° F. for 25 min. The garments were steam pressed.

Evaluation of Garments after Wear

Evaluation of the worn garments by the wearers and staff is shown in Tables II, III, IV, and V. Each of the garment properties that were evaluated is discussed in the following paragraphs. These properties were evaluated in order to determine the effect of wear.

The crease retention of all worn garments was generally satisfactory throughout the wear periods. The wearers' rating of garment crease retention ranged from unacceptable to good, fair retention being the opinion most often expressed for both laundered and drycleaned garments (Table II). In the opinion of the staff, crease retention never reached an unwearable condition on any garment.

Crease retention of the drycleaned garments was consistently rated higher than that of the laundered garments by both staff and wearers (Tables III, IV, and V). Statistical analysis of staff individual garment ratings has shown significant differences between the laundered and drycleaned garments after wear and cleaning. The drycleaned slacks were rated as superior in crease retention to the laundered garments by the wearers in 35 of 50 comparisons.

Shape retention of the worn garments after wear was judged by the amount of bagginess at knee and seat areas. The majority of the wearers rated loss of shape as "slight" to "moderate" after 150, 300, and 450 hr. of wear; after 600 hr. of wear, shape retention was most often judged to be "moderate" to "poor." Median staff ratings indicated only a slight change from the original appearance throughout the study (Table V).

The wearers' evaluations indicate that the drycleaned slacks had better shape retention than the laundered garments (Table III). In contrast, the staff found little differences in shape retention between the laundered and drycleaned garments (Tables IV and V), which indicates that loss of shape may have been more obvious when the garments were being worn.

Both the staff and the wearers rated wrinkling on a majority of the garments as slight to moderate throughout the study (Tables II and V). Table III

TABLE II. Wearers' Modal Rating of Garment Performance after Wear

Property	150 Hr. wear 0 Cleaning		300 Hr. wear 1 Cleaning		450 Hr. wear 2 Cleanings		600 Hr. wear 3 Cleanings		750 Hr. wear 4 Cleanings	
	L*	DC*	L	DC	L	DC	L	DC	L	DC
Crease retention										
Sharpness of front crease after wear	fair	fair	fair	fair	fair	fair	fair	fair	poor	poor
Shape retention										
Loss of shape at knees and seat after wear	slight	slight	slight	slight	moderate	slight	moderate	moderate	moderate	moderate
Wrinkle resistance										
Wrinkling after wear	moderate	moderate	moderate	moderate	moderate	moderate	moderate	moderate	moderate	moderate

* Code: L—laundered garments; DC—drycleaned garments.

TABLE III. Wearers' Evaluation of Garment Performance after Wear

Property	150 Hr. wear 0 Cleaning 25L*–25DC*			300 Hr. wear 1 Cleaning 20L–20DC			450 Hr. wear 2 Cleanings 15L–15DC			600 Hr. wear 3 Cleanings 10L–10DC			750 Hr. wear 4 Cleanings 5L–5DC		
	L	DC	NP*	L	DC	NP	L	DC	NP	L	DC	NP	L	DC	NP
	Number preferring:			Number preferring:			Number preferring:			Number preferring:			Number preferring:		
Overall preference	4	0	19	2	15	3	1	13	1	0	9	1	0	5	0
Crease retention	6	3	12	3	13	3	0	11	4	2	7	1	0	3	2
Shape retention	8	6	8	2	11	7	1	10	4	2	6	2	0	3	2
Wrinkle resistance	1	0	21	1	2	17	0	5	10	1	1	8	1	1	3
Fabric surface changes	Number observing:			Number observing:			Number observing:			Number observing:			Number observing:		
Fuzz increase	8	7		9	4		8	6		7	3		3	1	
Pills	0	1		4	2		6	4		3	2		0	0	
Softer fabric	Number rating:			Number rating:			Number rating:			Number rating:			Number rating:		
	3	3	14	10	1	7	11	0	2	8	0	2	5	0	0

* Code: L—laundered garments; DC—drycleaned garments; NP—no preference between garments.

indicates that the wearers noted few differences in wrinkling between the worn garments. However, in matched-pair analysis the staff ranked the laundered garments as having better wrinkle resistance than the drycleaned garments (Table IV).

Wrinkling was rated by the staff, not only as to the number of wrinkles present, but also as to the heaviness or sharpness of the wrinkles in the crotch and seat areas of each garment. In most cases it appeared to the staff that both laundered and drycleaned garments had approximately the same number of wrinkles, but that those observed in the drycleaned slacks were sharper and more noticeable. Since the wearers were given no special instructions for the evaluation of garment wrinkling, their judgments may not have been as critical as those of the staff.

Increases in the amount of fuzz on the fabric surfaces of the garments were very small throughout the study (Table V). However, analysis of matched-pair rankings by the staff have shown statistically significant differences between laundered and drycleaned garments at all wear levels over 300 hr. (Table IV). Fabric fuzz level of a drycleaned garment was never higher than that of the corresponding laundered garment after 300 hr. of wear. In contrast, differences between laundered and drycleaned garments were not shown by wearers' ratings or by staff median ratings.

Although pills were noted by the staff on 72% of the garments in this study, the staff median ratings for pill formation (Table V) were very low. The poorest rating given an individual garment was 3.1, indicating a moderate amount of pill formation (borderline acceptability). The presence of pills was reported by few of the wearers, probably because of the low level of pilling on the majority of the gar-

ments. However, Table III indicates that of those wearers reporting pills, they were found more frequently on the laundered than on the drycleaned slacks.

Staff rankings of matched pairs has also shown that the severity of pilling was greater on the laundered slacks than on the drycleaned garments after wear and cleaning (Table IV). Pills were found on 80% of the laundered slacks, in contrast to 64% of the drycleaned garments. Pills appeared on the laundered garments at an earlier level of wear and cleaning in 12 of the 25 matched pairs, while on only three matched pairs did pills appear first on the drycleaned garments.

Variations were noted in the number of hours a garment was worn before pill formation was first observed. For example, pills developed on the garments worn by one man after only 150 hr. of wear, while in another case pills were not observed until after 750 hr. of wear. This seems to indicate that the formation of pills on these garments may have been affected by individual characteristics of the wearers.

Staff rankings of matched pairs of slacks indicated a relationship between increases in fabric fuzz level and pilling propensity (Table IV). Richardson et al. [3] has reported that pills result from the raising of a fuzz on fabric surfaces.

Another fabric surface characteristic, abrasive wear, was evaluated by the staff and the wearers. After 750 hr. of wear, only very slight evidences of abrasive wear were found on the garments. Therefore, no comparison between the two methods of maintenance could be made for this characteristic.

TABLE IV. Staff Evaluation of Garment Performance after Wear; Number of Superior Garments in Matched-Pair Rankings

	150 Hr. wear 0 Cleaning 25L*–25DC*			300 Hr. wear 1 Cleaning 20L–20DC			450 Hr. wear 2 Cleanings 15L–15DC			600 Hr. wear 3 Cleanings 10L–10DC			750 Hr. wear 4 Cleanings 5L–5DC		
Property	L	DC	ND*	L	DC	ND	L	DC	ND	L	DC	ND	L	DC	ND
Crease retention	8	11	6	1	19	0	0	15	0	0	10	0	0	5	0
Shape retention	10	14	1	4	12	4	4	9	2	4	5	1	2	2	1
Wrinkle resistance															
Crotch	11	7	7	15	3	2	13	2	0	8	1	1	2	1	2
Seat	9	10	6	12	4	4	10	0	5	7	1	2	4	0	1
Fabric surface changes															
Pills	2	2	21	3	10	7	0	11	4	0	8	2	0	5	0
Fuzz	7	3	15	5	4	11	0	10	5	0	8	2	0	4	1

* Code: L—laundered garments; DC—drycleaned garments; ND—no difference between garment rankings.

TABLE V. Staff Median Ratings * of Garment Performance after Wear

	150 Hr. wear 0 Cleaning 25L†–25DC†		300 Hr. wear 1 Cleaning 20L–20DC		450 Hr. wear 2 Cleanings 15L–15DC		600 Hr. wear 3 Cleanings 10L–10DC		750 Hr. wear 4 Cleanings 5L–5DC	
Property	L	DC	L	DC	L	DC	L	DC	L	DC
Crease retention	2.4	2.4	2.6	2.3	2.6	2.2	2.8	2.4	2.8	2.3
Shape retention	2.4	2.3	2.2	2.0	1.9	1.8	2.0	1.8	2.3	2.3
Wrinkle resistance										
Crotch	2.8	2.8	2.6	2.7	2.4	2.6	2.5	2.7	2.5	2.7
Seat	2.7	2.7	2.4	2.6	2.5	2.6	2.6	2.6	2.5	2.6
Fabric surface changes										
Pills	1.0	1.0	1.1	1.0	1.1	1.0	1.2	1.0	1.2	1.0
Fuzz	1.2	1.2	1.2	1.3	1.3	1.2	1.3	1.3	1.4	1.3

* Median ratings: 1.0—no change from original appearance; 2.0—slight change from original appearance; 3.0—moderate change from original appearance; 4.0—objectionable change from original appearance; 5.0—unwearable condition.

† Code: L—laundered garments; DC—drycleaned garments.

The amount of lint adhering to the garments also was evaluated by the staff, but since a negligible amount was observed, no comparison was possible.

In order to obtain an evaluation of fabric hand changes, we asked the wearers to indicate the "softest" of the two garments. After the first cleaning, the laundered slacks were selected as being softer than those that had been drycleaned in all but 12 of the 50 evaluations (Table III). Since before the first cleaning the wearers did not indicate any difference in softness between the slacks, apparently the first cleaning produced a significant change in fabric hand. This change may have been a factor contributing to the differences noted between the slacks after cleaning in crease retention, shape retention, and wrinkle resistance.

The final item of the questionnaire asked the wearers to indicate a preference between their two garments. The drycleaned slacks were more often preferred to the laundered garments after all cleanings. All five wearers preferred the drycleaned slacks after 750 hr. of wear and 4 cleanings.

Evaluation of Worn Garments after Wear and Cleaning

Both staff and wearers evaluated every garment after each cleaning for crease retention, shape retention, and wrinkle resistance. The majority of the wearers judged their garments to have from good to excellent crease retention after cleaning and pressing. Those wearers who noted a difference in sharpness of front crease between their garments at this time consistently specified a preference for the drycleaned garment.

The creases of the home laundered and pressed slacks were judged by the staff to be slightly less sharp than those of the original garments, while the creases of the drycleaned garments were equal in sharpness to those of the original garments. This difference in sharpness of crease may account, at least in part, for the superiority of the drycleaned garments in crease retention found at the end of the wear periods. Neither staff nor wearers noted differences in wrinkle resistance or shape retention between the laundered-pressed and drycleaned-pressed garments. The staff considered all garments to be equal in appearance to the original slacks for both of these properties.

The laundered garments also were evaluated by the staff before pressing. In the opinion of the staff evaluators, the slacks were not acceptable for wear without pressing, because of seam puckering and poor crease retention. After the first laundering, staff median ratings ranged from moderate to objectionable loss of front creases. An objectionable loss of crease, as compared with original creases, was noted on all garments after 5 launderings. On the other hand, loss of shape in knee and seat areas was judged to be very slight after all launderings. Fabric wrinkling after tumble drying and before pressing was negligible throughout the study.

Seam puckering of the laundered garments before pressing was pronounced, but this was reduced considerably by home pressing. Seam puckering was also observed on the drycleaned and pressed garments; however, this condition was never as evident on the drycleaned garments as it was on the home laundered and pressed slacks.

Dimensional changes of the garments were negligible throughout the study. Mean values for garment shrinkage were never greater than 2%, regardless of the method of maintenance.

The laundering procedure used effectively avoided fabric wrinkling, making pressing of the fabric *per se* unnecessary. However, poor crease retention and pronounced seam puckering after the laundering procedure necessitated pressing the garments.

Conclusions

The 65% Dacron/35% rayon gabardine slacks used in this wear study were found to be generally serviceable during wear. In only a few cases were the slacks rated by either the wearers or the staff as being unacceptable for any property evaluated.

The drycleaned garments received higher staff and wearer ratings more often than did the laundered garments. The cost of maintenance was not considered in this investigation, and if actual maintenance costs were calculated, it would be expected that drycleaning would be the more expensive process. However, the importance of maintenance costs in relation to garment appearance can be decided only by the individual consumer.

The garments were not found to meet the requirements of a wash and wear, or minimum care item, as described in the literature [1, 2], since loss of crease

and seam puckering, resulting from home laundering, necessitated thorough pressing after each washing.

Some of the men were consistently harder on their garments than were others. At each wear level the garments were returned in varying physical conditions, ranging from heavy to light wear. These differences occurred despite the fact that the wearers were selected from a professional group engaged in similar type work. There was no apparent connection between age or size and the wear habits of the individual. It appears that it is important to consider these differences in wear habits when investigating fabric and garment serviceability by means of wear studies.

Acknowledgment

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Part II: Laboratory Evaluation

Abstract

Physical measurements were made on a minimum care Dacron[1] and rayon blended fabric to determine the effect of maintenance and wear on serviceability. The fabric had been worn and home laundered, worn and commercially drycleaned, and commercially drycleaned without wear.

Physical changes in the fabric, as measured in the laboratory, were generally consistent with an earlier subjective evaluation of the fabric. Physical characteristics of the fabric, with the exception of stiffness and abrasion, showed only slight changes.

An ideal procedure for the determination of fabric or garment serviceability involves the evaluation of performance by means of a wear study. In such a study the fabric is subjected simultaneously to a combination of destructive factors under end-use conditions. In contrast, laboratory measurements are generally made under artificial conditions, and only one deleterious factor is evaluated at a time. These measurements are useful for comparative purposes, but the correlation between such measurements and fabric performance under actual wear conditions may be poor or unknown. Despite the acknowledged merit of wear studies, their use has been limited because of prohibitive cost. Expense factors involved include the cost of fabric and garment construction, the replication necessary for reliable results, and the long period of time needed to produce significant garment degradation. Standard laboratory procedures therefore have been established which attempt to predict garment performance, and these methods are commonly used as a substitute for serviceability studies. However, the introduction of a new textile product on the market, such as minimum care garments, frequently necessitates the use of the wear study technique in order to determine the extent to which standard laboratory methods will predict garment serviceability.

The role of maintenance is one of the important factors to consider in the over-all serviceability, or performance, of all clothing. A serviceable garment must be able to withstand renovation without excessive fabric damage. In addition, minimum care garments should show little or no change in appearance with proper maintenance methods. Poor methods of maintenance may cause serious damage to many garments; however, the extent of degradation occurring under ideal maintenance conditions needs further investigation.

The results of the subjective evaluation of mini-

[1] Du Pont trademark.

mum care men's slacks during 750 hr. of wear have been previously reported [4]. In this study two methods of maintenance were employed; home laundering and commercial drycleaning. While the garments were found to be generally serviceable, the results of the wear study indicated differences between the drycleaned and laundered garments. In most cases the drycleaned garments were preferred to the laundered garments by those participating in the wear study. Laboratory measurements were made on fabrics which had been worn and home laundered, worn and commercially drycleaned, and commercially drycleaned without wear. These measurements were made to determine the effect on fabric properties of the two methods of maintenance when combined with wear, and also the effect of drycleaning *per se,* on the fabric properties measured.

Procedure

Characteristics of the blended fabric of 65% Dacron and 35% rayon used in all slacks have been described previously, as have been the methods of maintenance and the wear study procedure [4]. Seventy-five garments were purchased and divided into three sets: 25 were worn and home laundered; 25 were worn and drycleaned; and 25 were drycleaned without wear. Two identical garments, one from the set to be home laundered and the other from the set to be drycleaned, were issued to each of the 25 participants in the wear study. All worn garments were cleaned after each 150-hr. wear period. The set of garments that was not worn was drycleaned with the worn garments. After each cleaning, five garments from each set were withheld from wear for laboratory analysis. Laundered and unworn garments were not included in the design of the study because of the added expense involved.

The sampling plan was designed in such a manner that half of the samples were taken from areas of the garments where heavy wear was anticipated, and half from areas of less intense wear, with the exception of the edge abrasion samples. This was done in an attempt to obtain a representative over-all value for the various laboratory measurements. At every wear level 2 samples per garment were taken for each fabric measurement, providing 10 samples from each set of garments. Four samples were taken from each garment for yarn measurements, giving a total of 20 samples from each set. Samples for each laboratory measurement were taken from the same relative positions on all garments, regardless of size.

Measurements of fabric weight, crease recovery, yarn strength and elongation, fabric strip strength and elongation, and colorfastness to light were made according to standard and tentative ASTM procedures [2]. Flex stiffness was measured in accordance with Method 5206, Federal Specification CCC-T-191b [6]. Fabric thickness was measured with a "Compressometer" as described by Schiefer [5], using a foot 1 in. in diameter and a pressure of 1 lb./sq. in. All physical measurements on fabric and yarn were made under standard atmospheric conditions (70° F. ± 2°; 65% RH ± 2%).

Resistance to both flex and edge abrasion was measured on the Universal Wear Tester. Flex abrasion was measured by the ASTM method [2], using a 1½-lb. head weight and a 5-lb. tension weight. Resistance to edge abrasion was measured by means of the attachment supplied with the Universal Wear Tester. Samples for this measurement were taken from the back cuff edges of the garments. The edge abrasion attachment was placed so that the longer dimension was parallel to the front of the instrument; the reciprocating table was held stationary; the specimens were clamped with the folding plate inside the fabric; a 1-lb. head weight and "0" abrasion paper were used; abrasion was continued until all fibers in the abrasion area were worn off, actuating an electrical relay and stopping the machine.

Dimensional stability of the original fabric was measured according to Method 5552, Federal Specification CCC-T-191b [6]. The garments were measured before wear, and before and after each cleaning, to the nearest ⅛ in. at the waist, hips, front rise, back rise, inseam, and outseam.

Evaluations of the fabric for color changes after wear and cleaning were measured on a Gardner Automatic Color Difference Meter, using the R_d scale and Munsell color paper 5YR 3/2 for instrument standardization [3]. The percentage of nonfibrous material present on the garments was determined in accordance with the procedure outlined in AATCC Tentative Test Method 20-53 [1].

The laboratory data collected in this study were subjected to statistical analysis by the use of standard deviations and analyses of variance.

Discussion

The laboratory measurements performed may be separated into two general categories: those that provided descriptive fabric information and those

which gave information more closely related to the functional properties of this fabric when used in minimum care men's slacks. Those measurements related to the functional properties of the fabric are discussed below, and the mean values of pertinent laboratory measurements only are shown in Table I.

The stiffness of the fabrics, as measured by the cantilever test, was found to decrease with wear and the maintenance methods used. The decreases in warp stiffness were found to be significantly greater for the laundered garments than for the drycleaned garments (Table I). One drycleaning resulted in approximately a 1% increase in warp stiffness, while one home laundering decreased warp stiffness approximately 30%. The second home laundering produced another significant decrease in warp stiffness. Additional launderings caused only small changes, but after five launderings a total decrease of approximately 44% in warp stiffness had occurred. In contrast, there was no large decrease in warp stiffness of the drycleaned garments until after the fifth cleaning, at which time a cumulative percentage decrease of 29% was found. The relationship among filling stiffnesses of the three garment sets was similar to that found in the warp measurements, although in every case the filling decrease was considerably greater. Both maintenance methods produced large decreases in filling stiffness after the first cleaning. Apparently wear alone had little effect on fabric stiffness, since small differences were generally found between garments that had been worn and drycleaned and those that had been drycleaned and not worn. Despite these differences in fabric stiffness that appeared between the two methods of maintenance, no significant changes in crease recovery were found (Table I).

The amount of nonfibrous material in the fabric was found to decrease after repeated cleanings, and the losses of the laundered garments were greater than those of the drycleaned garments. The original fabric was found to contain 8.1% by weight of nonfibrous material; the presence of a urea-formaldehyde resin finish was indicated by the proposed ASTM method, Appendix VII [2]. After 750 hr. of wear and 5 drycleanings, approximately 7.3% of the total fabric weight was found to be of a nonfibrous nature. The garments that were drycleaned without wear showed a loss similar to that of the drycleaned and worn garments. After 5 cleanings they contained 7.6% nonfibrous material. However, after the garments had been home laundered 5 times, 6.6% nonfibrous material was present. It seems possible that the loss of nonfibrous material may be related to the losses of fabric stiffness found among the three garment treatments.

All garments were found to be relatively stable

TABLE I. Mean Values of Certain Physical Properties of Fabric

Hours wear	Fabric strength, dry, lb.		Fabric elongation, dry, %		Flex abrasion, cycles		Edge abrasion, cycles	Flex stiffness, face up, in.-lb.		Crease recovery, %	
	Warp-wise	Filling-wise	Warp-wise	Filling-wise	Warp-wise	Filling-wise	Warp-wise	Warp-wise	Filling-wise	Warp-wise	Filling-wise
0	152.2	78.3	85	55	986	1599	2550	3.78×10^{-4}	4.63×10^{-4}	84	78
150											
DCO*	154.2	78.8	80	54	2057	2435	2595	4.10×10^{-4}	1.55×10^{-4}	81	76
DC	158.4	75.6	86	53	2096	2848	2516	3.82×10^{-4}	1.50×10^{-4}	75	71
L	157.4	76.1	92	55	3960	7110	1989	2.65×10^{-4}	1.50×10^{-4}	83	75
300											
DCO	154.9	76.2	81	53	1288	2048	2908	4.31×10^{-4}	1.53×10^{-4}	78	75
DC	151.1	78.0	83	53	1295	1698	3173	4.09×10^{-4}	1.73×10^{-4}	78	73
L	158.2	71.6	89	53	4523	8837	1453	2.05×10^{-4}	1.03×10^{-4}	80	75
450											
DCO	153.4	77.2	82	54	1490	2322	2937	5.68×10^{-4}	2.40×10^{-4}	80	74
DC	151.6	75.9	85	52	2289	3522	2078	3.73×10^{-4}	1.72×10^{-4}	79	76
L	150.4	74.6	89	54	4611	8483	1739	2.20×10^{-4}	0.98×10^{-4}	82	75
600											
DCO	159.6	74.8	83	54	3218	5742	1907	3.60×10^{-4}	1.40×10^{-4}	82	77
DC	147.8	73.5	80	51	1501	1880	2040	3.40×10^{-4}	1.40×10^{-4}	80	75
L	151.5	74.4	89	54	5028	9920	1312	2.10×10^{-4}	1.00×10^{-4}	83	79
750											
DCO	156.2	76.1	83	53	2863	4654	1651	3.00×10^{-4}	1.50×10^{-4}	81	75
DC	151.7	72.8	82	50	2870	4214	1604	2.70×10^{-4}	1.10×10^{-4}	81	75
L	154.4	69.4	86	50	4554	8988	1139	2.10×10^{-4}	0.90×10^{-4}	85	79

* Code: DCO—garments drycleaned without wear; DC—drycleaned garments; L—laundered garments.

dimensionally, and neither maintenance method produced significant changes in fabric weight or thickness. Dimensional change varied in different areas of the slacks; seam puckering was a contributing factor, in all probability, since the greatest shrinkage occurred at the front rise, inseam, and outseam of the garments (Table II). While all changes observed were small, never exceeding a mean of 2% at each wear level, the greatest shrinkage was found on the laundered garments. Dimensional change of the original fabric, as measured in the laboratory, was less than 1% in both warp and filling directions.

The durability of the fabric, as measured by yarn and fabric strength and resistance to abrasion, was excellent throughout the study. After 750 hr. of wear and 5 cleanings, the strength of yarn and fabric was essentially unchanged from that of the original. Changes in fabric and yarn elongation were insignificant, except in the case of warp fabric elongation. The laundered and worn garments tended to have higher warp fabric elongation values than the drycleaned slacks.

There was a decided increase in flex abrasion for all fabrics after the first cleaning; these increases remained constant during repeated wear and cleanings. The increase was considerably greater for the laundered garments than for the drycleaned slacks. After 750 hr. of wear, the increase for the laundered slacks was approximately 362%, while the drycleaned garments showed an increase of only 191%.

In contrast, the resistance of the fabric to edge abrasion decreased with wear and cleaning. A significant decrease in resistance to edge abrasion of the laundered garments followed the first cleaning, while the resistance to edge abrasion of the drycleaned garments was not noticeably reduced until 4 cleanings and 600 hr. of wear. The decrease after 750 hr. of wear was approximately 55% for the laundered garments, while a 37% decrease was found on the drycleaned garments. With both types of abrasion there was little difference between the garments that were drycleaned and worn and those that were drycleaned and not worn. Therefore, it appears that the changes found in resistance to abrasion were due to maintenance and not wear.

Measurement of the resistance of the fabrics to flat abrasion was not completed because anomalous wear patterns were consistently obtained. This difficulty was apparently due to inherent fabric properties and not to operator or instrument variables, since the latter factors were carefully controlled.

The fabric was found to be colorfast to laundering and drycleaning in both Stoddard and perchlorethylene drycleaning solvents. However, after 20 hr. of exposure in the Fadeometer a "just appreciable" fading was observed.

Conclusions

The results of laboratory measurements and subjective evaluations of the garments were in general agreement. In the opinion of wearers and staff the slacks were generally acceptable for wear throughout the study. The fabric was not found to be deficient in any physical property measured.

Loss of fabric stiffness was the difference most frequently observed by the wearers between the laundered and drycleaned garments. Since the laundered slacks were consistently rated by the wearers as being softer than the drycleaned slacks, and at the same time a preference for the drycleaned garments was indicated, it appears that loss of fabric stiffness was a contributing factor in determination of garment acceptability. Laboratory measurement of fabric stiffness also showed a significant difference between the laundered and drycleaned garments, indicating a good correlation between objective and subjective evaluation of fabric stiffness.

There was agreement between the wearers' evaluation of wrinkle resistance and laboratory measurement of crease recovery, since both rated all garments as being acceptable. The loss of fabric stiffness of the laundered garments did not significantly affect fabric crease recovery.

TABLE II. Mean Percentage Dimensional Change of Garments

Treatment	Waist	Hips	Front rise	Back rise	Inseam	Outseam
5 Drycleanings 0 Hr. wear	−0.62	−0.84	−0.45	−1.72	+0.17	0.00
5 Drycleanings 750 Hr. wear	+0.68	−0.89	−0.96	+0.98	+0.33	−0.18
5 Launderings 750 Hr. wear	+0.22	−0.58	−1.74	−0.28	−1.22	−0.70

The elimination of seam puckering and the improvement of crease retention after home laundering would greatly improve the serviceability of these minimum care garments. While these properties are not measureable by any present standard laboratory procedure, visual evaluation after treatment by the specified laundering method will give an indication of garment performance in these areas. In this study, the first home laundering and drycleaning indicated the presence of these deficiencies.

Degradation of this fabric due to wear was negligible as measured by both subjective and laboratory methods. Since no differences were found between the drycleaned and worn garments and those garments drycleaned without wear, it can be assumed that the differences found are the result of the two methods of maintenance used. If the control garments, those drycleaned and not worn, had not been included in the study, the changes observed in the worn garments would have been erroneously interpreted as being the result of wear and not of maintenance.

Acknowledgment

This study was made possible through the cooperation of the University of California and the California State Board of Dry Cleaners.

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Correction

In the article, "The Effect of Temperature on the Rate of Creep Failure for 66 Nylon," by Bernard D. Coleman (Textile Research Journal, May 1958) Equation 15 on p. 398 should read as given below.

$$\log_{10} t_b = -17.85 \pm 0.75 + (8.45 \pm 0.26)\frac{10^3}{T}$$

The Application of Spot Tests in the Examination of Synthetic Fibers[1]

Part I

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THE USE of experiences and points of view characteristic of the *Chemistry of Specific, Selective, and Sensitive Reactions* [2] has proved of great value in studies relating to the development of inorganic and organic spot test analysis. Very considerable advances have been accomplished in the past five years, especially in the field of organic spot test analysis, through the working out of new procedures for the so-called preliminary examination and also through the evolution of new tests for functional groups and procedures for detecting or identifying individual compounds [3]. In the course of these studies it became evident that spot tests in their original form or in appropriate modifications can frequently be called on in the chemical examination of textile materials. It seemed probable that synthetic fibers would be a suitable area for this type of study, in which the objective is the development of new micromethods of characterization and identification. What follows constitutes the first report of our findings.

Test for Nitrogen-Bearing Synthetic Fibers by Pyrolytic Oxidation

Since some synthetic fibers contain nitrogen while others are free of this element, a test for nitrogen obviously provides a means of distinguishing between these classes. For many years it has been the practice to use the classic Lassaigne test [10], in which the sample is fused with an alkali metal to yield alkali cyanide. The latter is then detected by conversion into Prussian blue, or the hydrocyanic acid is released by means of an acid and then identified by characteristic reactions. The fusion with alkali metals requires special care in macro-, semimicro-, and microanalysis, and since additional steps are necessary for the detection of cyanide or hydrocyanic acid, the procedure is not only dangerous but time-consuming. Moreover, the Lassaigne test is not absolutely reliable, since it fails with some nitrogenous materials or succeeds only with considerable amounts of the sample [1].

It has been found in this laboratory that nitrogen can be detected without fail in organic compounds by a new micro test [6]. Trials have shown that this procedure is well suited for the examination of synthetic fibers. The basis of the test is that all organic (also inorganic) compounds of nitrogen yield nitrous acid when heated with ignited manganese dioxide (Mn_2O_3). This gaseous product can be detected with high sensitivity in the gas phase by the familiar Griess reaction (red color formation in an acetic acid mixture of sulfanilic acid and 1-naphthylamine). As little as 0.2–0.3 μg. of nitrogen can be detected within about 2 min. in any organic compound by means of pyrolytic oxidation. Accordingly, tiny amounts of synthetic fibers are sufficient for this test for a possible content of nitrogen.

Procedure

The test is conducted in a micro test tube which projects through a perforated sheet of asbestos. A little of the specimen is placed in the test tube and intimately mixed with about 0.2 g. of MnO_2 or Mn_2O_3. The mouth of the test tube is covered with a disk of filter paper moistened with the Griess reagent and the bottom of the tube is strongly heated with a micro flame. In general, 1–2 min. heating is enough. If nitrogen is present, a red or pink circle develops on the colorless paper.

Reagents

The Griess reagent is prepared just before use by mixing equal volumes of 1% solution of sulfanilic acid in 30% acetic acid and 0.1% solution of 1-naphthylamine in 30% acetic acid. If preferred, the 1-naphthylamine may be replaced by N-(1-

[1] Translated by Ralph E. Oesper, University of Cincinnati.

naphthyl) ethylenediamine dihydrochloride, as recommended by B. E. Saltzmann [11]. The red color is more stable than that produced by the Griess reagent.

A strong nitrogen reaction was secured by this procedure from the following types of synthetic fibers:

Polymers of ε-aminocaproic acid

BASF Perlon W type	Perlon Caprolaktam BASF
BASF Perlon B type	Perlon, Vereinigte Glanzstoff-Fabriken A.G.

Hexamethylene adipamide

Nylon

Acrylonitriles

Orlon [2] 41	Verel (Acrylic) (Eastman)
Orlon [2] 42	DNA Acrylic fiber (Goodrich)
X-51 Acrylic	Phrix, Gesellschaft m.b.H.
PAN fiber (Cassella)	Creslan or X-54
Acrilan	Darlan
Dynel	

As expected, the following types of synthetic fibers gave a negative response to the test for nitrogen:

Polyester fibers

Dacron [2]	Terylene

Polyvinylchlorides

PCU	Vinyon HH

Detection of Acrylonitrile Fibers by Pyrolytic Formation of Thiocyanic Acid

Accordng to Heyn [9], the acrylonitrile fibers are polymers of acrylonitrile (vinyl cyanide), either the pure polymer Orlon (E. I. du Pont de Nemours) or a copolymer. Copolymers are with vinyl chloride (Acrilan, Chemstrand Corporation; Dynel, a crimped staple fiber, and Vinyon N, a continuous filament, both manufactured by Union Carbide and Carbon) or with acrylamide (X-51, in 1952 an experimental fiber of American Cyanamid Co.).

For the characterization of acrylonitrile fibers a new test for aliphatic and aromatic cyanides (nitriles) can be used [8]. The test is based on the fact that volatile thiocyanic acid is split off when aliphatic and aromatic cyanides are strongly heated with sulfur. Thiocyanic acid can readily be identified with great sensitivity by the well-known color reaction with ferric salts.

[2] Du Pont trademark.

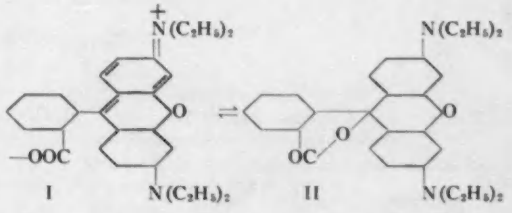
Procedure

The test is conducted in a micro test tube which projects through a perforated sheet of asbestos. A little of the specimen is placed in the test tube and intimately mixed with several cg. sulfur. The mouth of the test tube is covered with a disk of filter paper moistened with concentrated acidified ferric chloride solution. It is advisable to start heating at the top of the micro test tube because of the sublimation of sulfur. The bottom is then strongly heated with a micro flame. A positive response of the test is indicated by a deep red circle on the yellow paper.

Detection of the Acrylamide Component in Acrylonitrile Fibers through Chemical Adsorption of Rhodamine B

Among the acrylonitrile fibers and among the synthetic fibers noted above, those fibers containing acrylamide differ in a characteristic manner as regards their behavior toward the red aqueous solution of rhodamine B or the colorless benzene solution of this dye. In both cases, there is an almost instantaneous appearance of an intense red coloring, which is not removed by rinsing with water or benzene. The effect is particularly striking when the benzene solution is used, since a red reaction product is given by two colorless components.

The basis of the color reaction is a chemical adsorption of rhodamine B from its water or benzene solution. The former contains the red quinoid ions (I), the latter contains the isomeric lactone form (II) of the dyestuff.



The chemical adsorption involves a salt-like bonding of the basic rhodamine B on the surface of the fibers through the acidic hydrogen atoms of the acrylic acid amine residing there.

$$CH_2 = CH - CONH_2 \text{ or } CH_2CH - \underset{\underset{OH}{|}}{C} = NH$$

The adsorbate exhibits the color and fluorescence of the benzene-soluble salts of rhodamine B with complex metallo-halogeno acids [5] or with azinitro compounds [7], but it differs from them through its insolubility in benzene. This case is analogous to the production of aluminum-8-hydroxyquinolate as an individual phase and to the chemical adsorption of hydroxyquinoline and its derivatives on the surface of alumina [4]. In both of these latter instances the salt-like bonding of the hydroxyquinoline on the aluminum atoms results in products of analogous color and fluorescence, but these products differ in that only the salt but not the adsorption compound (or complex) is soluble in chloroform.

Procedure

A little of the sample is placed in a micro test tube and three or four drops of a saturated colorless benzene solution of rhodamine B added. If the response is positive the red color appears almost instantly. It is well to wash the tinted product with benzene and place it on filter paper. Against this white background, it is easy to discern both the red color and the orange-red fluorescence under the ultraviolet lamp.

Immeasurably small amounts of the X-51 fiber will give a positive test.

Acknowledgment

We thank Professor A. N. J. Heyn of Clemson College for providing experimental material and valuable information.

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Conference On Radiation and High Temperature Behavior of Textiles

November 14–19, 1958

A two-day conference, titled as above, will be held at the New York Academy of Sciences, 2 East 63rd Street, New York City, under the auspices of the Academy, The Polytechnic Institute of Brooklyn, and the U. S. Navy Clothing and Textile Research Laboratory. Eleven papers will be delivered. For further information write to J. J. Press, U. S. Navy Clothing and Research Laboratory, Brooklyn 32, New York.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the Journal. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the Journal is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Iodine Sorption Values of Some Chemically Modified Cottons

Southern Regional Research Laboratory [1]
New Orleans, Louisiana
April 9, 1958

To the Editor

Textile Research Journal

Dear Sir:

In the course of another investigation involving iodine sorption measurements on partially acetylated cottons, some comparative iodine sorption data were obtained for a group of cyanoethylated yarns and for several cotton sheeting samples which had been treated with beta-propiolactone.

The cyanoethylated yarns, ranging in nitrogen content from 2.1 to 7.2%, were the same as those recently investigated by Mazzeno et al. [4]. Cyanoethylation of the yarn was carried out by immersing the cotton, impregnated with 60% add-on of 2% sodium hydroxide solution, in commercial grade acrylonitrile at 60 ± 1° C.

The beta-propiolactone (BPL) fabrics were of two types: those boiled under reflux in a xylene solution of beta-propiolactone (4.8–47.8% add-on) and those soaked in 15% sodium hydroxide followed by treatment with dilute solutions of beta-propiolactone (5.0–16.3% add-on). In both methods the samples were subsequently freed from unbound polymer and by-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

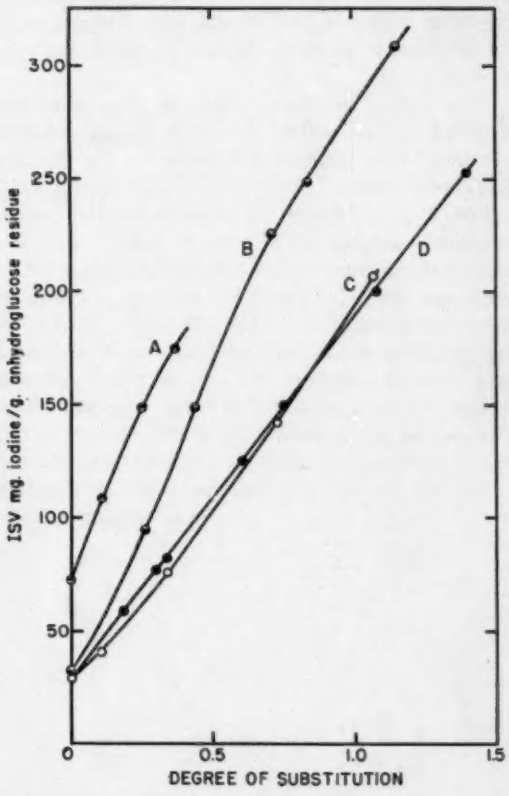

Fig. 1. Iodine sorption values as related to the degree of substitution for chemically modified cottons. (A) BPL-treated (15% NaOH method), (B) cyanoethylated, (C) BPL-treated (xylene-reflux method), (D) partially acetylated.

products. Some of the properties of these samples and the corresponding controls, which were subjected only to refluxing in xylene or soaking in sodium hydroxide, are listed in the first table of the recent publication by Reinhardt et al. [5].

The iodine sorption measurements were made by a modification [1] of the method of Schwertassek [6, 7]. The iodine sorption value (ISV) is defined as the number of milligrams of iodine sorbed per gram of anhydroglucose residue.

The results are shown in Figure 1, in which the iodine sorption values are plotted against the degrees of substitution. The published data for partially acetylated cotton samples [1] have been included for comparison. The horizontal-axis designation is not strictly applicable to the BPL-treated samples, since all the lactone groups are not necessarily attached directly to the cellulose. BPL tends to form polyesterified grafts [2, 3, 5]; therefore the degree of substitution is probably somewhat lower than indicated.

The iodine sorption values of the chemically modified cottons increased with the degree of substitution. The increase was linear for the partially acetylated cottons.

For a given degree of substitution the cyanoethylated samples sorbed more iodine than the acetylated samples—about 50% more over most of the range studied. The BPL samples prepared by the xylene-reflux method had almost the same sorbing capacities as the corresponding acetylated samples. Those prepared by the sodium hydroxide method had very much higher iodine sorption values. This can be attributed in part to the increase caused by the pretreatment with 15% sodium hydroxide and in part to the fact that the two methods result in different products and different degrees of polymerization [2, 5]. Thus, the sodium hydroxide treatment resulted in a control having an ISV of 70 instead of 30, and the increase in ISV with the degree of substitution was greater for the xylene-reflux samples.

The results show in general that the iodine sorption values of these chemically modified cottons depend not only upon the substituent and the degree of substitution, but also, in the case of the BPL-treated cottons, upon the method of preparation.

Acknowledgments

The authors are grateful to Laurence W. Mazzeno, Jr. and Robert M. Reinhardt for supplying the cyanoethylated and beta-propiolactone-treated cottons.

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